NOUVELLE THEORIE DES PLAISIRS,

Par Mr SULZER, *de l'Academie Royale des Sciences & Belles-Lettres de Berlin;*

AVEC

DES RÉFLEXIONS

Sur l'Origine du Plaisir,

Par Mr. KAESTNER de la même Académie.

Vero fruere non superbus gaudio.
MARTIAL.

M. DCC. LXVII

DES PLAISIRS. 155

vement de vibration, qu'ils confervent pendant un temps fenfible; les nerfs ne font point des cordes tendues, ni des corps rigides. Car dans ce cas, une feule impreffion momentanée feroit durer les fenfations, ce qui répugne à l'expérience. En effet dès qu'on ferme l'œil, dès qu'on bouche l'oreille, les fenfations ceffent. Au lieu qu'elles continueroient, fi les nerfs avoient un mouvement fenfible de vibration (*)

(*) Cette fuppofition paroît confirmée par une expérience affez curieufe. Si l'on joint deux pieces, l'une de plomb & l'autre d'argent, de forte que les deux bords faffent un même plan, & qu'on les approche fur la langue on en fentira quelque goût, affez approchant au goût de vitriol de fer, au lieu que chaque

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Sur ces remarques fe fonde mon fecond principe général, favor : *que toute fenfation totale eft compofée d'un grand nombre de fenfations momentanées qui fe fuccedent avec une rapidité à ne point laiffer entrevoir les momens de temps qui s'écoulent d'un coup à l'autre.*

Partant maintenant de ces deux principes, il me femble qu'il n'eft plus fort difficile d'ex-

piece à part ne donne aucune trace de ce goût. Il n'eft pas probable que, par cette jonction des deux métaux, il arrive quelque folution de l'un ou de l'autre, & que les particules diffoutes s'infinuent dans la langue. Il faut donc conclure, que la jonction de ces métaux opere dans l'un ou l'autre, ou dans tous les deux, une vibration dans leurs particules, & que cette vibration, qui doit néceffairement affecter les nerfs de la langue, y produit le goût mentionné.

THE FIRST SUGGESTION OF THE VOLTAIC CELL

[Fac-simile pages from Sulzer's book, 1767. See foot-note (*).]

THE VOLTAIC CELL:

ITS CONSTRUCTION AND

ITS CAPACITY.

BY

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PREFACE.

THE most important problem now before the electrical investigator is the production of cheap electricity. The principal modes by which this may be attained are, first, improvements in steam boilers and engines, gas-engines, and other existing transformers of power; second, the utilization of natural powers, such as waterfalls, currents, tides, the wind, solar heat, etc.; and third, the electro-chemical decomposition of cheap or refuse substances in the voltaic cell. To the electrical student the last is the most inviting and equally the most promising in the possibilities which it offers. Nature has already marked the end of the path along which the advance must be made by the capabilities which she has given to the animal organism of converting chemical energy into other forms of energy with the minimum loss in the form of heat. When carbon is economically burned in the voltaic cell, the era of cheap electricity will have arrived; and when this is done through the combination of that carbon with the oxygen of the air, perhaps the *ultima thule* in point of cheapness, as well as of the reign of steam, will be reached.

The object of the present work is to assist the student and investigator in this undertaking by placing before him the record of the principal discoveries and researches relating to chemical generators of electricity, descriptions of many (not all, for their name is legion) of the most distinctive and ap-

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proved types of cells, and the latest knowledge as to their efficiency, measurement, and modes of use.

The number of sources laid under contribution is large. Chief among them is Dr. D. Tommasi's recent treatise, "Les Piles Electriques," from which copious extracts have been translated. The extensive electrical library collected by the author and now known by his name has been freely drawn upon, especially for the valuable information contained in the older and rarer works regarding the labors of Volta, Galvani, Aldini, Ritter, Erman, Sturgeon, Cruikshank, Bunsen, Daniell, and the earlier investigators. Especial acknowledgments are due to the published Transactions of the American Institute of Electrical Engineers, to the files of the *Electrical Engineer* and the *Electrical World*, to Mr. Edward Weston, and to the excellent treatises of Mr. Carl Hering, Mr. W. T. A. Emptage, Professor W. Larden, Professors Ayrton and Perry, Mr. J. T. Niblett, Messrs. Slingo and Brooker, besides many others which have been consulted as occasion required.

NEW YORK, February, 1893.

THE VOLTAIC CELL.

CHAPTER I.

THE BEGINNING OF THE VOLTAIC CELL.

IN the year 1767 there was published, probably in Paris (although no place is named on its title-page), a little work entitled " Nouvelle Théorie des Plaisirs, par M. Sulzer de l'Académie Royale des Sciences et Belles-lettres de Berlin." The preface states that its contents had been read in the form of memoirs before the learned society named. Its æsthetical philosophy is that all pleasure is merely relative, and that supreme enjoyment is only attained by those who have endured trouble and vexation—which last, it is believed, is not wholly out of accordance with the experience of many people who labor in the electrical field. In discussing phenomena which affect the senses the author says :

" How is it possible to explain the action of odoriferous substances or of savors, if not by a succession of impulses? A single particle striking but once can excite only a momentary sensation, and therefore reiterated impacts are necessary in order to produce a lasting impression. It cannot be said that the nerves receive a movement of vibration which they retain for a perceptible time : they are neither tense nor rigid bodies. In that case, a merely momentary impression would produce sensations of long duration, which is contrary to experience. In fact, when the eye or ear is closed, sensations end, instead of continuing as would be the case did the nerves have a sensible

movement of vibration." In support of this theory, that all sensation is due to a vast number of momentary impressions succeeding one another with great rapidity—the analogue of the corpuscular theory of light—Sulzer adds in a foot-note the following remarkable passage :

"If two pieces of metal, the one of lead and the other of silver, be joined together in such a way that their respective edges may form but one plane, and if they be thus placed on the tongue, a taste will be perceived quite similar to that of vitriol of iron ; nevertheless, if either of these pieces of metal be separately applied, no vestige of such a taste is left. It is not probable that by the junction of these two metals any solution of either occurs, or that the dissolved particles insinuate themselves into the tongue. It must therefore be concluded that the junction of the metals causes in one or the other, or in both, a vibration of their particles, and that this vibration necessarily affects the nerves of the tongue and produces the taste mentioned."

This statement—and even in the light of our modern hypotheses it may well be regarded as extraordinary, for more than one reason *—is the beginning of our knowledge of the voltaic cell ; and, like the first announcements of most important discoveries, it remained unnoticed and unknown for many years. The fact seems to have been rediscovered by Humboldt in 1799, for he describes the same experiment, and then, curiously enough, adds to each plate a long iron wire. " By passing the wires," he says, " in a parallel direction through a door behind which they are brought together and separated alternately, the person who makes the experiment ascertains, by the taste he feels on the tongue, the situation of the extremity of each of the wires." Literally, a foretaste of the telegraph. The discovery was again made by Volta, and it was announced at the time when the conflict between himself and his great rival, Galvani, was at

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* " We have the strongest reason for believing that what the nerves convey to the brain is, in all cases, motion. It is the motion excited by sugar in the nerves of taste which, transmitted to the brain, produces the sensation of sweetness, while bitterness is the result of motion produced by aloes."—TYNDALL.

its height.   He noticed "that a ' coating of the nerve ' applied
to the point or to the inferior surface of the tongue and a
'coating of the muscle' applied to the superior excite, the in-
stant they are brought into contact, an acidulous taste similar
to the one which is perceived after the tongue is burned."   The
world, even at that early day, had determined to call all these
phenomena by Galvani's name whether they were justly attribu-
table to him or not—a predilection of which it is only just be-
ginning to become cured.   And, therefore, this particular oc-
currence discovered first by Sulzer, again by Humboldt, and
again by Volta, is called by Wilkinson, writing in 1804, " the
galvanic taste."

The story of Galvani and his frogs is known to every school-
boy and needs no repetition here.   Like all popular legends, it
has been greatly distorted, and perhaps has tended rather to
obscure the brilliancy of Galvani's fame than to enhance it.
The man was a cautious and skilful investigator, and had his
life been spent outside of the arena of scientific controversies
or been less embittered by personal misfortune he would have
left mankind owing him even a greater debt than it now does.
But whether history will give him the eminence which his own
contemporaries accorded him is doubtful.   The smoke of the
conflict, now nearly a century old, between the believers in the
chemical theory and the adherents of the contact theory has not
yet cleared away, nor can that controversy yet be said to have
definitely ended.   But enough issues have been settled, enough
facts are undisputed, to make it plain to the student that, for
the practical electro-chemical cell as we know it to-day, the
palm belongs to Volta and not to Galvani ; and that the terms
" Galvanism " and the " Galvanic battery," like " Franklinism "
and the " Franklinic current," are ultimately to be detached
from the phenomena to which they have been applied, and
thrown aside with the husks of discarded names which strew
the pathway along which physical science advances.

Galvani describes his discovery of what he always called " ani-
mal electricity " in his famous *De Viribus Electricitatis* of 1791
in the following words : " It is principally found in the nerves

and in the muscles, and its path seems to be from the muscles
to the nerves, or rather from the nerves to the muscles, by the
shortest route, as in the Leyden jar. . . . There is in every part
a double electricity, positive and negative and disjunctive . . .
One exists internally in the muscles, the other externally ; so
that the muscular fibre acts like a little Leyden jar, and the
nerves simply serve the office of conductors." The term "gal-
vanic phenomena," almost at the beginning, was applied to the
property which the nerves were said to possess of becoming
irritated by the contact of living organs and metallic substances
or substances containing charcoal. The substances which
were applied to animal matter were known as "coatings;" and
these, says Reinhold, in his *Geschichte des Galvanismus,* 1803,
being "applied to a part of an animal capable of being incited,
give motion to the galvanic fluid by embracing it in some way
or other." He divides the coatings into two classes—the
"nervous," which are applied to the nerves, and the "muscular,"
which are applied to the muscles—and even, after the fashion
of nowadays, represents these by letter symbols ; as CM, CN.
The cause of the phenomena observed was "a galvanic fluid " ;
but the term was not generally accepted. Creve prefers
" metallic irritation ; " Fowler, simply " influence ; " and Car-
radori, " nervous fluid."

Meanwhile, people began to recognize the function of dif-
ferent parts of the apparatus. The first division made was
that between " exciters " and " conductors ; " the exciters in-
cluding the substances which, united together, produce the
galvanic phenomena, and the conductors those " which, while
not exciting the galvanic phenomena, offer no obstacle to their
manifestation." It was observed that the several parts of the
apparatus stood in series relation one to the other ; for the con-
ductor was connected to one coating, which in turn made con-
tact with the animal matter, which in turn made contact with
the other coating, which was finally joined to the conductor.
Humboldt calls this " the galvanic chain ; " Reinhold, " the
galvanic ring ;" Wilkinson, " the galvanic circle." In 1798,
Halle differentiated this circle into two parts ; namely, the

"animal arc," which is formed by the organs of the animal, and the "exciting arc," which is composed of the coatings in the conductor. But note the theory. Some fluid exists in the living flesh. Irritate the flesh and it is made to appear. No wonder that all Europe depopulated the frog-ponds. The conditions which Charles Lamb so wittily describes in his essay "On Roast Pig" were all here repeated; and the Chinese who burned their pigsties for the sake of the crackling of the succulent porker found their imitators in the European philosophers who ravaged the swamps and the marshes for the material wherewith to make their electrical generators. And yet, during the same year that Galvani's famous Latin work appeared, another scientific student, long unknown to fame and scarcely recognized any more than Sulzer is nowadays, wrote to the Scientific Academy of Florence concerning experiments which he had made with metals that he had plunged into water, and said that he was convinced "that a chemical action had taken place, and that it was unnecessary to seek elsewhere the nature of the new stimulus; . . . that it was manifestly owing to the slow combustion and oxidation of the metal; which combustion must have been accompanied by an attraction of oxygen and by a disengagement of light and caloric." Those were wonderful words uttered by Fabroni, but, like many another discoverer, in saying them he committed the crime of being ahead of his time, and therefore they were buried out of sight in musty archives—the usual penalty inflicted by the world for such temerity, even when it considerately refrains from starving the discoverer.

But perhaps Fabroni's voice was lost amid the clamor of the conflict which soon began. "The new principle of artificial electricity discovered by me," says Alexander Volta of Pavia, "is the force and virtue of metals and charcoal in exciting and expelling the electric fluid by the means of a simple contact with all humid bodies which become, by this quality, so many conductors. . . ." Thus in the Philosophical and Medical Journal of Leipsic of 1793, and again in the Philosophical Transactions of the same year, he says: "We ought

rather to say we disturb the equilibrium of the electric fluid than restore it, in that it flows from one part to another of a nerve or muscle, etc., as well interiorly by their conducting fibres as exteriorly by means of applied metallic conductors; not in consequence of a respective excess or defect, but by an action proper to those metals when they are of different kinds. It is thus that I have discovered a new law, which is not so much a law of *animal* electricity as a law of *common* electricity ; to which ought to be attributed most of the phenomena which would appear from both Galvani's experiments and mine to belong to a principal spontaneous animal electricity, and which are not so, but are really the effects of a very weak, artificial electricity." And then later, in his famous memoir to the French National Institute of 1801, he describes his "electro-motive apparatus." It is made, he says, " in the form of a pile or of a range of cups . . . and consists in the simple metallic pair of plates composed of two different metals, and not in a humid substance applied to a metallic substance or comprised between two different metals. The humid layers in a compound apparatus of this description are therefore merely intro-duced to establish a reciprocal communication between all the metallic pairs of plates, so arranged as to impel the electric fluid in one particular direction ; or, in other words, to make their communication in such a way that no part of the action should take a contrary direction." The zinc is to be laid over the silver, the moist pasteboard over the zinc, and so on, con-secutively. He called the different conducting substances the " motors," and their arrangement a " circle," in which " an electric stream is occasioned which ceases only when the circle is broken, and which is renewed when the circle is again ren-dered complete."

Such was the genesis of the voltaic cell, and such was the beginning of a conflict which has continued through the whole of the century now closing. "Voltaism," says Sturgeon, writ-ing in 1842, " is the production of electricity by the association of metals and other inorganic bodies . . . by the simple contact of inorganic bodies, whether solid or fluid ;" and galvanism is

the production of electrical effects "either by a natural or an artificial association of animal matter, whether alive or dead."

But the "animal matter" part was dropped out of the last definition by the majority of writers, and gradually the issues cleared and became formulated into what are now known as the "contact theory" and the "chemical theory" of the cell. The writers on electricity adopted one theory or the other at will, or else trimmed, and, after the fashion of De la Rive in 1853, defined the voltaic pile as "an apparatus in which electricity is developed, according to some, by the contact of two metals of a different nature, and according to others, by the chemical action of the liquids with which it is charged upon one of the two metals which enter into its formation." Perhaps the best statement of these two great theories is that given by Faraday, and is as follows:

"The contact theory [of the cell] assumes that when two different bodies being conductors of electricity are in contact, there is a force at the point of contact by which one of the bodies gives a part of its natural portion of electricity to the other body, which the latter takes in addition to its own natural portion; that, though the touching points have thus respectively given and taken electricity, they cannot retain the charge which their contact has caused, but discharge their electricities to the masses respectively behind them; that the force which at the point of contact induces the particles to assume a new state cannot enable them to keep that state; that all this happens without any permanent alteration of the parts that are in contact, and has no reference to their chemical forces (Exp. Res., 1840).

"The chemical theory [of the cell] assumes that at the place of action the particles which are in contact act chemically upon each other and are able, under the circumstances, to throw more or less of the acting force into a dynamic form; that, in the most favorable circumstances, the whole is converted into dynamic force; that then the amount of current-force produced is an exact equivalent of the original force employed; and that in no case (in the voltaic pile) can any

electric current be produced without the active exertion and
consumption of an equal amount of chemical force ending in a
given amount of chemical change (Exp. Res., 1840)."

The theory which to-day finds the most general acceptance
is by Gore thus excellently defined :

" The essential cause is the stored-up and ceaseless molecu-
lar energy of the corroded metal and of the corroding element
of liquid with which it unites, whilst contact is only a static
condition, and chemical action is the process or mode by which
the molecular motions of those substances are more or less
transformed into heat and current."

CHAPTER II.

GENERAL DEFINITIONS.

Electromotive Force (symbol E. M. F.) is defined by Maxwell (1881) as "whatever produces or tends to produce a transfer of electrification;" by Gore (1890) as "that . . . which moves or tends to move electricity from one place to another, and is in some sense analogous to pressure."

Current, says Faraday (1833), is "anything progressive, whether it be a fluid of electricity or two fluids moving in opposite directions, or merely vibrations, or, speaking still more generally, progressive forces."

An electrical element, couple, or pair consists of two bodies connected in an electrical conducting circuit between which two bodies exists a difference of potential, and between which the electromotive force due to that difference of potential is maintained by the expenditure of energy upon a part of the circuit, including and included between the bodies.

A voltaic element, couple, or pair is an electrical element in which the energy of chemical action is expended in maintaining the potential difference, and hence is converted into the energy of an electric current.

A voltaic cell is a combination containing an electrical element, means for converting the energy of chemical action into the energy of an electric current, and circuit connections so arranged that the combination itself forms a portion of the conducting circuit.

A primary voltaic cell is one in which the means for the development of the energy of chemical action is normally present and active or ready to act.

A secondary voltaic cell or voltaic accumulator is one in which

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the means for the development of chemical action is normally present, but is not active until so rendered by a chemical alteration produced by an electric current from another source.

A voltaic battery, primary or secondary, is two or more voltaic cells connected so as to deliver their currents upon the circuit.

Concerning the names of the parts of a voltaic cell much confusion has arisen. " Electrodes," " plates," " poles," " elements," are all used as interconvertible terms, though material distinctions are frequently drawn when the qualifying adjectives " positive" and " negative" are added. To get at the exact meaning it is therefore necessary to go down to the bedrock of Faraday.

" The general phraseology is," he says (Exp. Res., Jan. 1834, ¶661 *et seq.*), " that the positive pole *attracts* oxygen, acids, etc., or, more cautiously, that it *determines* their evolution upon its surface; and that the negative pole acts in an equal manner upon hydrogen, combustibles, metals, and bases. According to my view, the determining force is *not* at the poles, but *within* the body under decomposition ; and the oxygen and acids are rendered at the negative extremity of that body, whilst hydrogen, metals, etc., are evolved at the positive extremity.... The *poles*, as they are usually called, are only the doors or ways by which the electric current passes into and out of the decomposing body; and they, of course, when in contact with that body are the limits of its extent in the direction of the current. The term has been generally applied to the metal surfaces in contact with the decomposing substance ; but whether philosophers generally would also apply it to the surfaces of air and water against which I have effected electro-chemical decomposition is subject to doubt. In place of the term pole, I propose using that of *electrode* (ἤλεκτρον and ὁδός, a way), and I mean thereby that substance, or rather surface, whether of air, water, metal, or any other body which bounds the extent of the decomposing matter in the direction of the electric current. ... The anode is ... that surface at which the electric current ...

enters; it is the *negative* extremity of the decomposing body; is where oxygen, chlorine, acids, etc., are evolved, and is against or opposite the *positive electrode*. The *cathode* is that surface at which the current leaves the decomposing body and is its *positive* extremity; the combustible bodies, metals, alkalies, and bases are evolved there, and it is in contact with the *negative electrode*. . . . Many bodies are decomposed directly by the electric current, their elements being set free; these I propose to call *electrolytes.*"

The distinction drawn by Faraday between the surfaces of the decomposing body at which the current enters and leaves, and the surfaces or substances which not merely bound the extent of decomposing matter, but against or in contact with which the surfaces of the decomposing body exist, is very often entirely overlooked—with the consequence that the terms " positive electrode" and " negative electrode" are applied respectively to the anode and the cathode, as if the terms were synonymous, which is not strictly the case. This distinction will be clear from the diagram Fig. 1.
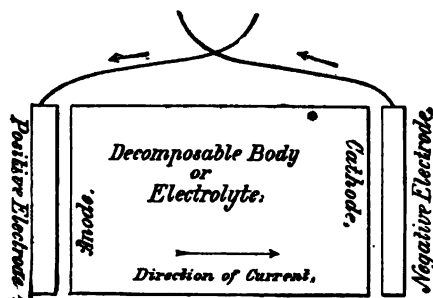
FIG. 1.

The positive electrode, therefore, is the substance or body with which the surface of the electrolyte whereat the current enters the electrolyte is in contact. It is the one from which the current moves within the cell. It is the zinc in the zinc-copper cell.

The negative electrode is the substance or body with which the surface of the electrolyte whereat the current leaves the electrolyte is in contact. It is the one toward which the current moves within the cell. It is the copper in the zinc-copper cell.

The *terminals* of a voltaic couple are those points whereat the electrodes are connected to the part of the circuit which is external to the cell. As the current in that part of the circuit moves apparently from the negative electrode to the positive one, the terminal of the negative electrode is sometimes called the *positive terminal* and that of the positive electrode the *negative terminal.*

The electrolyte is that body in the cell which undergoes decomposition and which also serves as a conducting medium for the current between the electrodes. If a liquid, it is frequently termed the "exciting liquid."

The path of the current, therefore, is inside the cell through the electrolyte and from the positive to the negative electrode, and outside of the cell through an external conductor leading from the positive to the negative terminal.

In a secondary cell, charged and active, and therefore, substantially, a primary cell, the same rules apply. During the charging of the cell the conditions are of course reversed, and the electrode which ultimately is negative is then positive.

Polarization is a condition due to the formation of a body, most commonly hydrogen, by electro-chemical decomposition upon the negative electrode, whereby a current in opposite direction to the normal current of the cell is produced, and through which the normal current may be greatly weakened. To remove this body by any suitable means, chemical or mechanical, is termed "depolarizing;" and if a chemical agent is employed for the purpose, it is called a "depolarizer." *A constant cell* is one in which polarization is reduced to a minimum or prevented. *A closed-circuit cell* is one in which the depolarizer acts so as practically to prevent polarization, in order that the cell may thus be left upon a closed circuit of moderate resistance for a long

time without much diminution of the current-strength. On the other hand, *an open-circuit cell* is one in which the depolarizer may be weak or absent, and which therefore is adapted to furnish current only at intervals and for short periods of time; the effects of polarization being eliminated while the cell is standing with the circuit open.

Local action is chemical action occurring within the cell, and is caused by the innumerable small currents which circulate between portions of the same electrode, as, for example, the zinc, due to differences between said portions in chemical or mechanical properties. In an open-circuit cell, therefore, it is advisable that means, such as amalgamation, should be provided for the elimination of local action.

The external resistance is the resistance in a circuit exclusive of that of the current generator. *Internal resistance* is that portion of the resistance of a circuit which exists within the generator.

The foregoing definitions have been prepared after a very careful consultation of all the principal authorities. It is unfortunate that there should have been in the past such wide differences as to the meanings of electrical terms as applied to the voltaic cell. For example, the word "element" is applied by Volta simply to a pair of plates. " The true element," he says, " of my electromotive apparatus consists in the simple metallic pair of plates composed of two different metals." Henry, writing in 1835, speaks of a battery as of " a single element or pair." De la Rive (1856) considers a voltaic pair to consist of two elements; and that seems to be the opinion of Wilkinson (1804), who defines primary exciters as "the elements of a voltaic couple." Maxwell (1873) uses the word "element" as synonymous with voltaic cell; and, after describing the purpose of the apparatus, says "this combination is called a cell or element of Daniell gravity." Professor Carhart (1891) apparently gives the term " element " a very limited signification, as he defines it as " a system of two different metals immersed in a liquid which acts chemically on one of them when the circuit is closed;" in which opinion he is ob-

viously not in accord with Professor Houston, who, in his Electrical Dictionary (1892), defines a voltaic element as " one of the two metals or substances which form a voltaic couple." An element, strictly speaking, is something which cannot be resolved into constituent parts or ingredients ; but the term, as electrically used and as applied to an electrical generator, means a combination of parts all of which are essential to the production of electricity. Such a generator is therefore, electrically considered, an indivisible element ; although, mechanically considered as a structure, it may be resolved into constituent parts.

The word " cell " is often used ambiguously, as witness the following passage from Maxwell : " A solution of sulphate of zinc is placed in a cell of porous earthenware, and this cell is placed in a vessel containing a saturated solution of sulphate of copper. A piece of zinc is dipped into the sulphate of zinc, and a piece of copper is dipped into the sulphate of copper. Wires are soldered to the zinc and to the copper above the surfaces of the liquid. The combination is called a cell or element of Daniell's battery," Here, obviously, the word is applied to the entire structure and also specifically to its containing vessel. The names that have been given to the voltaic cell and to the process of electrical generation therein are very numerous and very confusing. " Galvanic cell " and " galvanism " are still in current use. The " hydro-electric cell," the " galvanic circle," " galvanic plates," " chemico-electric cell," are terms frequently encountered. The word " pile " is used specifically to mean the column of superposed electrodes, such as that of Volta or Zamboni, or else is appropriated bodily from the French, where it means any kind of a cell. The confusing of the word " battery " with " cell " is of every-day occurrence ; and in fact, so far as relative usage is concerned, the term " battery " is employed in the majority of cases, whether we speak of one or more cells. Henry seems to have made the terms " battery " and " cell " synonymous, and for an assemblage of cells he uses the words " compound battery."

With regard to the names of the electrodes, the student of electrical literature must rely upon the context in order to determine which one is meant. Writers who lean to the contact theory of the cell are always inclined to look at it from the outside, and as there the current apparently moves from copper to zinc, they regard and call the copper the positive pole or · electrode, and the zinc the negative. Most French and German writers follow this rule—a fact which should be borne in mind in consulting their works. On the other hand, those who favor the chemical theory look at the decomposition of the electrolyte and the direction of the current therein, and give to the electrodes exactly the opposite names. This is the practice of most American and English writers. A distinction is also sometimes drawn between " electrode " and " plate." Thus, it is stated in Slingo and Brooker's " Electrical Engineering " (1890) : " The cell so acted upon became a secondary cell in which the negative electrode acted as the positive plate, being a sheet of lead with more or less complete film of gaseous hydrogen ; the other plate, or positive electrode, with its film of insoluble lead peroxide behaving as the negative plate." De la Rive calls the zinc in the cell both the positive metal and the positive or zinc pole ; the copper being termed the negative metal and the negative or copper pole. Nevertheless, he defines positive pole as " that extremity of the pole toward which the zincs of each pair are turned." Some writers prefer to call the cell terminals " rheophores "—a Greek name for which there is not the slightest necessity. Professor Carhart (1891) detaches the term " electrode " from the cell proper and applies it to the wires connected respectively with the zinc and copper plates. Henry defines a " deflagrator " as " several batteries united, the copper pole of the one with the zinc pole of another, and so on," and a " calorimotor " as " a battery in which one connector unites all the zinc, and the other all the copper " ; the cells, of course, being connected in one case in series, and in the other in multiple arc. The circuit connection whereby the cells were joined in the first instance were called by Henry an " alternate

or serial connector;" in the second case, a "homogeneous connector." Henry's connectors are sometimes confused with the "conjunctive wire" of Green (1827) and De la Rive (1853), which was the seat of what Oersted called "the conflict of electricity"—a phenomenon, by the way, which he pointed out (1820) as occurring not merely in that conductor, but "in the surrounding space."

CHAPTER III.

MEASUREMENTS.

UNITS OF MEASUREMENT.

Fundamental Units.—The fundamental units are those of *length, mass,* and *time.* Others are derived from these. The fundamental units used in electrical measurements are the second, the centimeter, and the gram.

The Second is the Unit of Time. Its value is the $\frac{1}{86400}$ part of the mean solar day.

The Centimeter is the Unit of Length. Its value is the $\frac{1}{100}$ part of a meter. The meter $= \frac{1}{10000000}$ part of the quadrant of a meridian of the earth.

The Gram is the Unit of Weight. It is the weight of one cubic centimeter of pure water at 4° C. (39°.2 Fahr.), the temperature of the maximum density of water.

The system based on these units is known as the centimeter-gram-second, or C. G. S., system.

Mechanical Units.—Of the mechanical units derived from the fundamental units above noted, the most important are the units of force and the unit of work.

The Unit of Force is the Dyne. It is the force which, acting on a mass of 1 gram for 1 second, generates in it a velocity of 1 centimeter per second. The acceleration due to gravity may be taken as 981 centimeters per second per second. That is, the unit of mass (1 cubic centimeter) is acted on by the earth's attraction with 981 units of force. Therefore 1 gram weighs 981 dynes, and 1 dyne = 1.0194 milligrams = .015731 grain.

The Unit of Work is the Erg. It is the work done by one dyne when it moves its point of application through a distance

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of 1 centimeter in the direction in which it acts. The erg is therefore the product of the unit of force—the dyne—and the unit of length—the centimeter.

The American and English Practical Work Unit—The Foot-pound. In American and English engineering practice the foot-pound is commonly employed as the practical unit of work. It represents the work done when a force equal to the weight of 1 pound moves its point of application through a distance of 1 foot in the direction in which it acts. As 1 cm. = .0328 foot and 1 gram = 981 dynes = .002204 pound, we have 1 foot = $\frac{1}{.0328}$ cm., 1 pound weight = $\frac{981}{.002204}$ dynes and 1 foot-pound = $\frac{981}{.002204}$ × .0328 erg = 1.356 × 10^7 ergs = .13825 kilogrammeter = .0018434 metric h.p. per second = .00181818 English h.p. per second = .0003264 calorie (kilo-cent.)=.0003767 watt-hour.

The French Practical Work Unit—The Kilogrammeter. In French practice the kilogrammeter is generally employed as the work unit and will be found most frequently referred to in the following pages. It represents the work of 1 kilogram in falling a distance of 1 meter. The kilogram therefore equals 9.81 × 10^5 dynes. Hence the kilogrammeter = 9.81 × 10^5 dynes × 10^2 = 9.81 × 10^7 ergs. The kilogrammeter therefore equals $\frac{9.81}{1.356}$ or 7.2314 foot-pounds = .01333 metric h.p. for one second = .013151 English h.p. for one second = .002361 calories (kilo-cent.) = .002725 watt-hour.

The Joule is a practical unit introduced simply for convenience because of the unwieldy smallness of the erg. It represents 10^7 = 10,000,000 ergs. Consequently, instead of writing the kilogrammeter = 9.81 × 10^7 ergs, or the foot-pound = 1.356 × 10^7 ergs, we may say the kilogrammeter = 9.81 joules and the foot-pound = 1.356 joules. The joule is therefore .73732 foot-pound = .102 kilogrammeter = .001359 metric h.p. for one second = .0013406 English h.p. for one second = .00024 calories (kilo-cent.) = .0002778 watt-hour.

The Unit of Power is the Watt, which is equal to the rate of doing the work of 1 joule per second = 44.239 foot-pounds per minute = 6.116 kilogrammeters per minute = .01444 calorie

(kilo-cent.) per minute = .001359 metric h.p. = .000134 English h.p. 1 kilowatt = 1000 watts.

The American and English Power Unit—The Horse-power. In American and English practice the horse-power is very commonly taken as the unit of power, and is the rate of doing work at 33,000 foot-pounds per minute or 550 foot-pounds per second. 1 horse-power = 745.9 $\times$ 10^7 ergs per second = 745.9 watts or 745.9 joules per second = 4562.3 kilogrammeters per minute = 10.77 calories (kilo-cent.) per minute = 1.0138 metric h.p. = .7459 kilowatt.

The French and German Power Unit—The Cheval-vapeur. In French practice the power unit is the metric horse-power or *cheval-vapeur* (sometimes written *force de cheval*) ; in German, *Pferdekraft.* It is the rate of doing work at 75 kilogrammeters per second = 75 $\times$ 9.81 $\times$ 10^7 ergs = 735.7 joules per second = 735.7 watts = 32549 foot-pounds per minute = 10.6 calories (kilo-cent.) per minute = .98634 English h.p. = .7357 kilo-watt.

There is a difference, therefore, of about ten watts between the French cheval-vapeur or metric horse-power and the English horse-power, which it is important to bear in mind in reading the results of French investigations.

The *cheval-heure* or metric horse-power hour represents the number of kilogrammeters furnished by 1 cheval-vapeur for 1 hour = 75 $\times$ 3600 = 270,000.

The Practical Unit of Heat is the Calorie. This is the amount of heat which will raise 1 gram of water from 0° C. to 1° C.—or (with sufficient accuracy) the product of the number of grams of water into the number of degrees centigrade through which they rise or fall in temperature. The term is often rendered doubtful from the fact that there are two calories, known respectively as the small calorie, for which Professor Lodge has proposed the term "therm," and the great calorie. The former is the one above defined ; the latter is the amount of heat required to raise the temperature of 1 kilogram of water from 0° C. to 1° C. and is that most generally used by French writers. 1 calorie (gram-centigrade) = .001 calorie (kilo-centi-grade.) The context easily indicates which calorie is intended.

1 calorie (kilo-cent.) = 4154.9 joules = 3063.5 foot-pounds =
423.5 kilogrammeters = .001569 metric h.p. hour = .0015472
horse-power hour = 1.1542 watt-hours.

   (The most complete tables of power units thus far pub-
lished will be found in Mr. Carl Hering's work on "Dynamo
Electric Machines," New York, 1890.)

   Electrical Units.—*Ohm's Law*, usually written (1) $C = \dfrac{E}{R}$,
expresses the relation of current (C), electromotive force (E),
and resistance (R) in the circuit. It is obvious that an ex-
pression for unity of any one factor can be obtained by making
the others equal to 1, and rewriting the above equation as

$$(2)\ \ E = CR \quad \text{and} \quad (3)\ \ R = \frac{E}{C}.$$

   Unit Current therefore [E and R being made equal to 1 in (1)]
is the current in a circuit with unit E. M. F. and unit resistance.

   Unit E. M. F. [C and R being made equal to 1 in (2)] is the
E. M. F. in a circuit with unit current and unit resistance.
Unit resistance [E and C being made equal to 1 in (3)] is the
resistance in a circuit with unit E. M. F. and unit current.

   Clearly, if the values of two factors are known, the other is
obtainable. The electrical units are derived from the C. G. S.
system of units, but are multiplied by integral powers of 10 for
convenience.

   The Unit of Current is the current which, flowing in a con-
ductor in the form of a circular arc one centimeter long, and
having a radius of one centimeter, acts with a force of 1 dyne
on a unit magnetic pole placed at the centre of the circle.

   The Ampere is the Practical Unit of Current and equals $\frac{1}{10}$
of the C. G. S. unit or 10^{-1} C. G. S. units. It is the current
given by 1 volt E. M. F. in a circuit of which the total resist-
ance is 1 ohm. The *ampere-hour* is the quantity of electricity
which traverses a conductor during one hour when the strength
of current is 1 ampere = 3600 coulombs.

   The Unit of E. M. F. is the E. M. F. that must exist between
two points when 1 erg of work is done per second for every
unit of current that passes between the two points.

The Volt is the Practical Unit of E. M. F., and is the É. M. F. which must exist between two points when a joule of work is done per second for every ampere passing between the two points. It equals 100,000,000 or 10^8 times the absolute unit of E. M. F. It is very nearly the E. M. F. of a cell consisting of a copper and a zinc plate immersed in a solution of zinc sulphate.

The Unit of Resistance is the resistance of a conductor such that when a unit of current flows steadily through it, its terminals are at unit of potential difference.

The Ohm is the Practical Unit of Resistance, and is the resistance of a conductor such that when an ampere flows steadily through it its terminals are at such potential difference that the E. M. F. b●tween them is one volt. It is the resistance of a column of mercury at 0° C. of 1 sq. mm. section and nearly 105 cm. in length : very nearly the resistance of a pure copper wire 1 mm. in diameter and 48 meters in length, or of an iron wire 4 mm. in diameter and 100 meters in length. It is 1,000,000,000 (or 10^9) times the absolute unit.

The Relations of the Electrical Units in C. G. S. Units are therefore, by Ohm's law,

$$C = \frac{E}{R}, \quad \text{or} \quad 10^{-1} = \frac{10^8}{10^9}.$$

The Unit of Quantity is the quantity which passes between two points in one second when unit current is flowing between them. *The Practical Unit of Quantity is the Coulomb*, which, defined with reference to the ampere, is $\frac{1}{10}$ the C. G. S. unit. This quantity—one coulomb—of electricity performs a definite amount of electrolysis in its passage through an electrolyte : it liberates a definite mass of each *ion*. If this be expressed in grams, the number is called the electro-chemical equivalent of that ion. It is usually given in milligrams. (See table, p. 24).

The expressions *ampere* and *coulomb per second* mean the same thing. The ampere-hour being the quantity of electricity which traverses a conductor during an hour, when the strength of current is 1 ampere, and the coulomb representing the quantity of electricity passing per second, it follows as before

stated that the ampere-hour = 3600 coulombs, and 1 coulombs = .00027 ampere-hour.

The Practical Unit of Capacity is the Farad.—It is the capacity of a condenser which, when charged with one coulomb of electricity, has a difference of potentials equivalent to an E. M. F. of 1 volt between its poles. Farad $= \dfrac{\text{coulomb}}{\text{volt}} =$ 10^{-9} C. G. S. units.

The following expressions are synonymous:

1 joule = 1 volt-coulomb = 1 watt per second = 1 volt-ampere per second.

1 watt = 1 volt-ampere = 1 joule per second = 1 volt-coulomb per second.

MEASUREMENT BY COMPUTATION.

Measurement of Energy.—When a current of C amperes runs between two points on a circuit, the difference of potential of which is E volts, then electrical energy disappears from these points at the rate of $C \times E$. Expressing C and E in amperes and volts, $EC =$ the volt-ampere or watt. English horse-power in round numbers therefore $= \dfrac{EC}{746}$, and metric horse-power (*cheval-vapeur*) $= \dfrac{EC}{736}$.

Measurement of Heat.—Joule showed experimentally that if a current C be flowing through a resistance R, then the heat evolved per second is proportional to the product C^2R, which expresses the heat-activity in watts. As 1 watt = .24 calorie (approx.) per second, this may easily be reduced to calories (gram-cent).

Distribution of Heat in the Circuit (Larden, 1888).—Let the current in a circuit be C; the resistances of battery and various parts of the current be $B . R_1, R_2, R_3,$ etc., respectively; the total resistance be R; the total heat evolved per second be H calories (gram-cent); the several portions evolved in the above different portions of the circuit be $H_B, H_1, H_2,$ etc., respectively. Then we evidently have the following relations holding:

$$\begin{cases} H = C^2R \times .24 = C^2(B + R_1 + R_2 + \text{etc.}) \times .24; \\ H_B = C^2B \times .24; \\ H_1 = C^2R_1 \times .24; \text{ etc.} \end{cases}$$

Whence also

$$\begin{cases} H_B : H_1 : H_2 : \ldots = B : R_1 : R_2 : \ldots; \\ H_B = \dfrac{B}{R} \cdot H; \\ H_1 = \dfrac{R_1}{R} \cdot H; \text{ etc.} \end{cases}$$

Numerical Examples (Larden).—(I) A battery has E. M. F. = 50 volts; the total resistance is 20 ohms. Find the current in amperes, and the activity (or work per second) in ergs per second, in watts and in horse-power.

Here

$$\begin{cases} C = \dfrac{E}{R} = \dfrac{50}{20} = 2\tfrac{1}{2} \text{ amperes}; \\ \text{activity} = CE = \tfrac{5}{2} \times 50 = 125 \text{ watts}; \\ \text{activity} = CE \times 10^7 = 125 \times 10^7 \text{ ergs per second}; \\ \text{activity} = CE \div 746 = \tfrac{125}{746} \text{ English horse-power.} \end{cases}$$

(II) In the same case the external resistance *Re* is 15 ohms, and the internal resistance *Ri* is 5 ohms. Find the external and internal activities both in watts and calories per second.

Here

$$\begin{cases} \text{external activity} = \dfrac{Re}{R} \times 125 = \tfrac{3}{4} \times 125 \text{ watts}; \\ \text{external activity} = \tfrac{3}{4} \times 125 \times .24 \text{ calorie per second}; \\ \text{internal activity} = \dfrac{Ri}{R} \times 125 = \tfrac{1}{4} \times 125 \text{ watts}; \\ \text{internal activity} = \tfrac{1}{4} \times 125 \times .24 \text{ calorie per second.} \end{cases}$$

(III) A battery has E. M. F. 20 volts and current 10 amperes.   Find the total heat per second in calories.

Here $H = C \times E \times .24 = 10 \times 20 \times 24$ calories per second.

MEASUREMENT BY ELECTRO-CHEMICAL EQUIVALENTS.

The electro-chemical equivalent of a substance is the quantity of the substance which is electrolyzed by one unit of electricity (one coulomb)—or it is, to quote Faraday, "a number representing the proportion in which an ion is evolved."   The quantity by weight of the substance is proportional to the strength of the current and may be ascertained by multiplying the chemical equivalent of the substance by the electro chemical equivalent of hydrogen.   In the following table this is done.

TABLE OF ELECTRO-CHEMICAL EQUIVALENTS.   (HOSPITALIER.)

Name of the substance.	Atomic weight.	Chemical equivalent.	Electro-chemical equivalent *e* in milligrams per coulomb.	Number of coulombs necessary to liberate one gram.	Mass liberated in one hour by a current of one ampere.
Hydrogen........	1.	1.	.0105	96,000	.0378
Potassium........	39.1	39.1	.4105	2,455	1.4680
Sodium...........	23.	23.	.2415	4,174	.8694
Gold.............	196.6	65.5	.6875	1,466	2.4750
Silver............	108.	108.	1.1340	889	4.0824
Copper, -ic salts...	63.	31.5	.3307	3,079	1.1900
" -ous salts.	63.	63.	.6615	1,540	2.3800
Mercury, -ic salts.	200.	100.	1.0500	960	3.7800
" -ous salts	200.	200.	2.1000	480	7.5600
Tin, -ic salts......	118.	29.5	.3097	3,254	1.1149
" -ous salts....	118.	59.	.6195	1,627	2.2298
Iron, -ic salts.....	56.	14.	.1470	6,857	.5292
-ous salts....	56.	28.	.2940	3,429	1.0584
Nickel......␣.....	59.	29.5	.3097	3,254	1.1249
Zinc.............	65.	32.5	.3412	2,953	1.2283
Lead.............	207.	103.5	1.0867	928	3.9041
Oxygen...........	16.	8.	.0840		
Chlorine.........	35.5	35.5	.3727		
Iodine............	127.	127.	1.3335		
Bromine.........	80.	80.	.8400		
Nitrogen.........	14.	4.3	.0490		

DETERMINATION OF E. M. F. OF CELLS BY THE METHOD OF THERMIC CONSTANTS. (D. TOMMASI, 1884.)

Single-liquid Cells.—In single-liquid cells the E. M. F. = the difference of the thermic constants (see table, p. 28) of the metal attacked and of the hydrogen disengaged divided by the volt expressed in calories.

If, for example, Ep represents the E. M. F. of a single-liquid cell, θ the thermic constant of hydrogen, θ' the thermic constant of the attacked metal, and V the volt expressed in calories, we have

$$
\begin{cases}
Ep = \dfrac{\theta_H - \theta'_{M'}}{V} \text{ (for monoatomic metals)}; \quad . \quad . \quad (1) \\[3mm]
Ep = \dfrac{\theta_{H^2} - \theta'_{M''}}{V} \text{ (for diatomic metals}; \quad . \quad . \quad . \quad (2)
\end{cases}
$$

V (volt) corresponds to 46.3 calories. (See page 86.)

To illustrate: in order to find the E. M. F. of a zinc-copper dilute sulphuric acid couple, we have, by (2),

$$
Ep = \frac{\theta_{H^2} - \theta'_{Zn}}{V} = \frac{2 \times 61.5 - 88.8}{46.3} = 0.7386 \text{ volt.}
$$

The E. M. F. of the same couple by direct experiment is found to be 0.81 volt.

The fact that the value found experimentally is greater than that indicated by theory is probably principally due to the action of the oxygen of the air on the hydrogen absorbed by the copper. This slow combustion of the hydrogen necessarily disengages heat, which, in becoming converted into electric energy, is added to and increases the intensity of the normal E. M. F. of the couple. In fact the E. M. F. developed by the action of zinc on dilute sulphuric acid varies not only with

the nature but with the physical state of the inactive metal : which explains why the E. M. F. of this couple has been found to differ by various investigators.

It follows from the preceding principle that the E. M. F. of the single-liquid cell is the same whatever may be the acid employed, and that it depends only on the attacked metal. An exception is, however, to be made in favor of acids which may be reduced by hydrogen—or, more exactly, by $H +$ cal, as would be the case with chromic or nitric acid, for example. Concerning these reductions, M. Tommasi states that they have hitherto been explained by assuming "a special and almost mysterious condition of the hydrogen, termed the 'nascent state,'" but that in 1877 he "demonstrated that hydrogen at the instant it quits a combination owes its reducing properties, not to its 'nascent state,' but to the quantity of heat which it disengages when set free."

Two-liquid Cells.—When a cell is formed of two metals, each placed separately in a solution of one of its own salts, and when these salts contain the same acid or the same halogen body, the E. M. F. of this couple is equal to the difference of the thermic constants (see table p. 28) of these metals divided by the volt expressed in calories or V.

θ and θ' expressing the thermic constants of the two metals M and M', and Ep the E. M. F. of the cell, we have

(1) $Ep = \dfrac{\theta_M - \theta'_{M'}}{V}$ (when the two metals are diatomic);

(2) $Ep = \dfrac{2\theta_M - 2\theta'_{M'}}{V}$ (when the two metals are monoatomic);

(3) $Ep = \dfrac{2\theta_M - \theta'_{M'}}{V}$

(4) $Ep = \dfrac{\theta'_M - 2\theta'_{M'}}{V}$

(when one of the metals is monoatomic and the other is diatomic).

Formula (3) may be used when the thermic constant of the monoatomic metal multiplied by 2 is greater than the constant of the diatomic metal, and (4) in the contrary case. Of the two metals, that of which the thermic constant is the lower forms the positive electrode of the element, while the other constitutes the negative electrode, which becomes enlargèd by the deposit due to the decomposition of its salt.

For example, to find the E. M. F. of the Daniell element : According to (1) the E. M. F. of this would be

$$Eb = \frac{\theta_{Cu} - \theta'_{Zn}}{V} = \frac{139 - 88.8}{46.3} = 1.084 \text{ volts.}$$

Calculated by the ordinary method of electro-chemical equivalents this is 1.16 volts.

The commonly accepted valuation of the E. M. F. of the Daniell element is 1.079 volts.

Comparing this, however, with the theoretic results of the two methods, it is evident that that obtained by the method of electro-chemical equivalents is 7.5 per cent too great, while that obtained by the method of thermic constants is in excess of the experimental determination by only 0.46 per cent.

The E. M. F. of all cells formed of two metals remains constant whatever may be the acid or the halogen body of their two salts.

Thus, for example, for à zinc-cadmium couple the E. M. F. will always be

$$Ep = \frac{105.4 - 88.8}{46.3} = 0.36 \text{ volt,}$$

whether the salts employed be sulphates, chlorides, acetates, etc.

TABLE OF THERMIC CONSTANTS.   (D. TOMMASI.)

General formula: $\Delta = \delta \pm \theta$.

Δ = salt of which the heat of formation is to be found ;

δ = heat of formation of the potassium salt having the same acid radical as the salt Δ ;

θ = thermic constant corresponding to the base of the salt Δ.

VALUE OF θ WITH RELATION TO THE MOLECULAR WEIGHTS OF THE DISSOLVED SALTS.

Salts of hydrogen or acids...	61.5 cal.
" " sodium	4.6
" " silver	87.4
" " thallium...........	62.3
" " magnesium	14.6
" " barium	$136.2 - x$*
" " strontium..........	6.0
" " calcium...........	14.0
" " zinc...............	88.8
" " cadmium...........	105.4
" " aluminium.........	43.3 or 3 $\times$ 43.3
" " manganese.........	73.6
" " iron (proto)........	101.6
" " iron (per).........	116.4 or 3 $\times$ 116.4
" " nickel	108.0
" " cobalt	106.8
" " copper	139 0
" " mercury...........	142.0
" " lead	123.2
" " tin................	120.4
" " tin (bi)	44.2
" " gold	147.0
" " ammonium	28.1

* x, calories of combination of barium with oxygen not yet determined.

HEATS OF FORMATION OF THE PRINCIPAL POTASSIC SALTS
IN SOLUTION ($H_2O = 18$).

	Molecular Formulæ.	Heats of Formation.
Fluoride of potassium..	FlK.............	98.4 cal.
Chloride " "	ClK.............	100.8
Bromide " "	BrK.............	91.0
Iodide " "	IK	74.7
Chlorate " "	ClO_3K.	96.0
Perchlorate "	ClO_4K.	96.4
Hypochlorite "	ClKO	91.9
Iodate "	IO_3K............	96.8
Nitrate '	NO_3K.....	96.1
Sulphate (neut.) "	SO_4K_2	196.0
Sulphate (acid) "	SO_4KH	96.0
Sulphite (neut.) "	SO_3K_2	196.4
Sulphite (acid) "	SO_3KH	98.9
Chromate "	CrO_4K_2..........	189.2
Bichromate "	$Cr_2O_7K_2$.	191.4
Acetate "	$C_2H_3O_2K$	95.6
Picrate "	$C_6H_2(NO_2)_3OK$....	95.9

To find, for example, the heat of formation of copper sulphate in solution, we have

$$\supset SO_4Cu = \supset SO_4K_2 - \theta.*$$

$$\supset SO_4Cu = 196.0 \text{ cal} - 139.0 \text{ cal} = \dot{}57.0 \text{ cal}.$$

As found by experiment this is 56.9 cal.

To find the heat of formation of chloride of zinc in solution we have

$$\supset Cl_2Zn = 2ClK - \theta.$$

$$\supset Cl_2Zn = 2 \times 100.8 \text{ cal} - 88.8 \text{ cal} = 112.8 \text{ cal}.$$

As found by experiment this is 112.8 cal.

*The sign $\supset$ placed before a salt indicates the heat of formation of the salt:

VARIOUS METHODS FOR DETERMINING THE E. M. F.
OF CELLS. (D. TOMMASI.)

Single-liquid Cells.—Let the couple, for example, be zinc-platinum and hydrochloric acid diluted.

Calorimetric Method.—Zinc plunged into hydrochloric acid is strongly attacked with the formation of chloride of zinc and disengagement of hydrogen, according to the equation

$$Zn + 2HCl = ZnCl_2 + H_2.$$
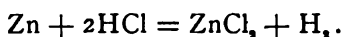
The calories produced in this reaction are equal to the calories of formation of the dissolved zinc chloride less the calories of decomposition of the hydrochloric acid also dissolved. Now HCl in decomposing into $H + Cl$ absorbs 39.3 calories, and chlorine in uniting with zinc disengages 112.8 colories. Hence the zinc platinum couple on contact with hydrochloric acid will give an E. M. F. equal to

$$112.8 - 2 \times 39.3 = \frac{34.2}{46.3} \quad \text{or} \quad 0.7386 \text{ volt.}$$

The volt corresponds to 46.3 calories.

Couples of which both metals are attacked by the exciting liquid.—Take, for example, the zinc-cadmium couple plunged into dilute hydrochloric acid. The E. M. F. is calculated as follows:

The E. M. F. of zinc is first determined as if it were the only metal attacked :

$$2HCl + Zn = ZnCl_2 + H_2 = \frac{34.2}{V} \text{ cal.}$$
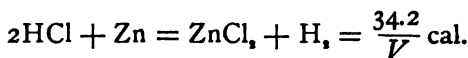
This operation is repeated for the other metal:

$$2HCl + Cd = CdCl_2 + H_2,$$
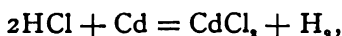
or

$$96.2^* - 2 \times 39.3 = \frac{17.6}{V} \text{ cal.}$$

---

* Heat of formation of dissolved cadmium chloride.

Hence the E. M. F. of the zinc-cadmium couple will be

$$\frac{34.2 - 17.6}{V} = \frac{16.6}{46.3} = 0.36 \text{ volt.}$$

The same result can be more simply obtained by the theory of substitutions by subtracting from the heat of formation of dissolved zinc chloride the heat of formation of dissolved calcium chloride, or

$$\frac{112.8 - 96.2}{V} = \frac{16.6}{46.3} = 0.36 \text{ volt.}$$

Method of Thermic Constants.—According to the general formula (see p. 25),

$$Ep = \frac{\theta_{H^2} - \theta'_M}{V},$$

we have for the zinc-platinum dilute hydrochloric acid couple

$$Ep = \frac{2 \times 61.5 - 88.8}{46.3} = 0.7386 \text{ volt.}$$

For the zinc-cadmium dilute hydrochloric acid couple we have

$$Ep = \frac{\theta_M - \theta'_M}{V} = \frac{105.4 - 88.8}{46.3} = 0.36 \text{ volt.}$$

(88.8 = thermic constant of zinc; 105.4 do. of cadmium; 61.5 do. of hydrogen. See table p. 28.)

Two-liquid Cells.—Two conditions are to be considered: (*a*) the two electrolytes are liquid; (*b*) one electrolyte is solid, the other liquid.

Calorimetric Method.—(*a*) The two electrolytes are liquid. Take the Daniell element, for example, which contains two liquids separated by a porous partition. It is necessary to consider:

1st. The action of the zinc on the dilute sulphuric acid.

2d. The action of the hydrogen on the sulphate of copper.

The zinc and sulphuric acid react in accordance with the following equation:

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$
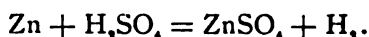
The calories disengaged in this reaction are equal to the calories of formation of the dissolved zinc sulphate, less the calories of decomposition of the sulphuric acid. Now, the calories of formation of the sulphate of zinc are equal to 107, and the calories of decomposition of a molecule of sulphuric acid into $H_2 + SO_4$ are equal, according to the law of thermic constants, to 73.0. Hence in the outer vessel of the Daniell cell there will be produced an E. M. F. equal to   .

$$107 - 73.0 = \frac{34.0}{V}.$$

On the other hand, the hydrogen due to the decomposition of the sulphuric acid goes over to the zinc sulphate in the porous cup and decomposes it in accordance with the following reaction:

$$H_2 + CuSO_4 = H_2SO_4 + Cu.$$
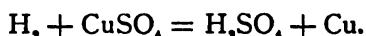
The calories disengaged by this reaction are found by subtracting from the calories of formation of sulphuric acid the calories of decomposition of copper sulphate, or

$$73.0 - 56.4 = \frac{16.6}{V} \text{ cal.}$$

The total E. M. F. of this couple is obtained by adding to the 16.6 cal the 34.0 cal previously found, or

$$\frac{16.6 + 34.0}{46.3} = 1.090 \text{ volts.}$$

The same result can be more simply obtained by taking the difference between the heats of formation of the dissolved sulphate of zinc and sulphate of copper, or

$$\frac{107 - 56.4}{46.3} = 1.090 \text{ volts.}$$

(107 = heat of formation of dissolved zinc sulphate ; 56.4 do. of dissolved copper sulphate.)

Method of Thermic Constants.—According to the general formula (see p. 25),

$$Ep = \frac{\theta_{Cu} - \theta_{Zn}}{V},$$

we have

$$Ep = \frac{139.0 - 88.8}{46.3} = 1.084 \text{ volts.}$$

Method of Electro-chemical Equivalents.—The general formula is

$$E = 4.16 \, ZQ,$$

in which

$Z =$ electro-chemical equivalent of the body liberated by the electrolyte.

$Q =$ quantity of heat in calories (gram-degrees) disengaged by one gram of this body in passing from the electrolyte to a state of chemical combination.

In the Daniell element two distinct actions occur : solution of the zinc in sulphuric acid, and deposit of copper due to the decomposition of the copper sulphate. There is therefore, on one hand, disengagement, and, on the other, absorption of heat, and the E. M. F. of the element is equal to the difference of the two actions.

Determining the first, that is, the heat disengaged per gram of zinc dissolved or 1670 calories,—Z being here equal to 0.0003412,—we have

$$Ed = 4.16 \times 0.0003412 \times 1670 = 2.37 \text{ volts.}$$

For the second, that is, the heat absorbed by the copper deposit, or 881 calories per gram,—*Z* being equal to 0.0003307, —we have

$$Ea = 4.16 \times 0.0003307 \times 881 = 1.21 \text{ volts.}$$

The E. M. F. of the Daniell element is therefore

$$Ep = Ed - Ea = 2.37 - 1.21 = 1.16 \text{ volts.}$$

(*b*) One of the electrolytes is liquid and the other solid. Let the couple be: zinc, diluted hydrochloric acid, porous cup containing solid lead chloride, and carbon.

In this couple, as in that of Daniell, there are produced two chemical actions : one in the external vessel, the other in the porous cup.   Consider these separately.

In the external vessel there is formation of zinc chloride and decomposition of hydrochloric acid ; whence

$$Zn + 2HCl = ZnCl_2 + H_2.$$
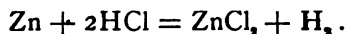
The E. M. F. resulting equals the calories of formation of the dissolved zinc chloride less twice the calories of decomposition of the dissolved hydrochloric acid, or

$$112.8 - 2 \times 39.3 = \frac{34.2}{V}.$$

On the other hand, in the porous cup there is decomposition of lead chloride and formation of hydrochloric acid.   This decomposition is produced by the hydrogen resulting from the reaction of zinc and hydrochloric acid in the external vessel, as is shown by the following equation:

$$PbCl_2 + H_2 = 2HCl + Pb.$$
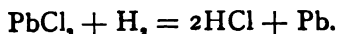
The E. M. F. generated in the porous cup is therefore equal to the calories of formation of the two molecules of HCl

less the calories of decomposition of one molecule of lead chloride.

$$2 \times 39.3 - 78.4 = \frac{0.02}{V}.$$

The total E. M. F. of the couple will then be

$$\frac{34.2 + 0.02}{46.3} = 0.73 \text{ volt.}$$

In this couple, as is apparent, the lead chloride serves only as a depolarizer for the negative electrode, without materially augmenting the E. M. F.

The E. M. F. of the couple can also be obtained by subtracting from the heat of formation of dissolved zinc chloride the heat of decomposition of solid lead chloride.

$$\frac{112.8 - 78.4}{V} = \frac{34.4}{46.3} = 0.74 \text{ volt.}$$

Method of Thermic Constants.—According to the general formula (see p. 27), we have

$$Ep = \frac{\theta_{Pb} - \theta'_{Zn}}{V} = \frac{123.2 - 88.8}{46.3} = 0.73 \text{ volt.}$$

It is to be noted, however, that if the electrolyte be completely insoluble in water—such as lead iodide, silver chloride, etc.—this formula is no longer applicable. Lead chloride is slightly soluble in water; nevertheless the thermic constant of lead has been calculated according to the heat of formation of dissolved lead chloride.

Method of Electro-chemical Equivalents.—The general formula

$$E = 4.16 \, ZQ$$

is employed as explained on p. 33.

MEASUREMENT BY INSTRUMENTS.

The usual instrumental methods of measurement are fully described in numerous standard text-books. (See " Practical Electricity," Ayrton, 1887; " Hand-book of Electrical Testing," Kempe, 1887; " Primary Batteries," Carhart, 1891 ; " Element-

ary Practical Physics," Stewart and Gee, 1891.) A brief description of the voltameter and its uses is given hereafter. Other modes are omitted here because the recent invention and introduction of the direct-reading instruments of Mr. Edward Weston have so simplified the various determinations as to render their use materially labor-saving in general practical work. The following explanation has been prepared by Dr. H. Maschke, and is furnished by Mr. Weston.

The Weston Voltmeter and Ammeter.—If a coil of wire carrying an electric current is brought between the poles of a horseshoe magnet, it behaves as if it were rigidly connected to a magnet fixed in its centre at right angles to the plane of its windings. Suppose the coil shown from above in Fig. 2 to be
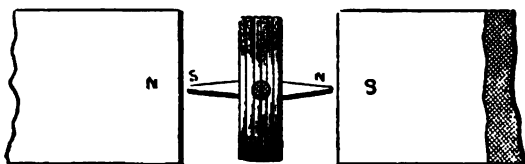

FIG. 2.—PRINCIPLE OF WESTON VOLT AND AMMETER.

suspended or pivoted so as to allow of its rotation around its vertical axis, and that it be traversed by a current having the direction of the small arrow. It will then have the polarity indicated.* If, however, it be traversed by a current in the opposite direction, Fig. 3, it will then be rotated in the direction
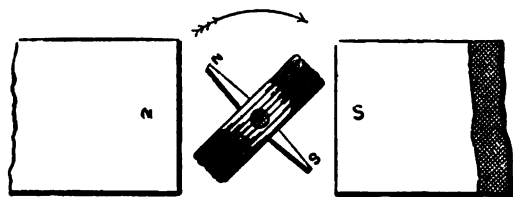
FIG. 3.—PRINCIPLE OF WESTON VOLT AND AMMETER.

of the larger arrow. This rotation will be produced even by the smallest current, provided the coil is not acted upon by some opposing force. To make it a measuring instrument, therefore, requires that the tendency to turn be opposed by

---

* That end of the solenoid in which as one faces it the current runs clockwise will be — or S. seeking, that end in which the current is counter-clockwise will be + or N. seeking.

some counter-force. Such a counter-force is introduced in the form of two flat, horizontal, spiral springs, fastened to the ends of the coil above and below it. When no current is flowing, these springs will keep the coil in a certain zero position, from which it will be deflected by a current traversing it to an extent bearing a relation to the difference of potential between the coil terminals. A pointer connected with the coil and moving over a properly graduated scale will then indicate the angular displacement of the coil, and, therefore, the pressure or strength of the current to be measured. This is the principle of the Weston voltmeter and ammeter.

The arrangement of the coil in relation to the magnet is shown in Fig. 4. The connections of the instrument are shown
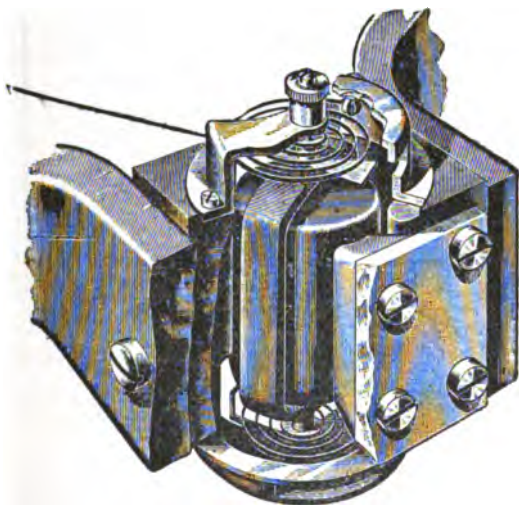
FIG. 4.—WESTON VOLT AND AMMETER—WORKING PARTS.

in Fig. 5. The current passes first through one spiral spring, then through the coil, and then through the other spiral spring. The voltmeter contains, besides the movable coil, a separate resistance-coil located under the scale-plate.

When the coil is in the zero position, the pointer, the normal direction of which is perpendicular to the plane of windings of the coil, forms an angle of 45 degrees with the middle line of the instrument. With the strongest current which is allowed

to pass through the instrument, the pointer is deflected 90 degrees from its zero position.   Beyond these two extreme positions the coil is allowed only a small range.

The scale is fastened to a brass plate, which is secured to the pole-pieces, projecting from them at right angles.   Below the scale, quite close to it, a mirror is attached, to enable one to avoid making an error in the reading, due to parallax.

The readings may be made immediately on applying the
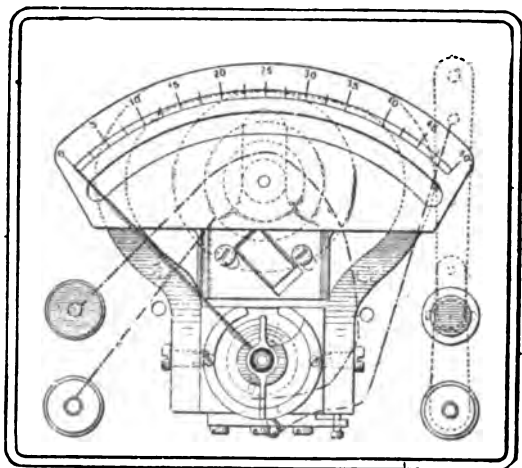
FIG. 5.—DIAGRAM OF CONNECTIONS, WESTON VOLT AND AMMETER.

current.   The pointer assumes its proper position by an instantaneous and dead-beat deflection.   It indicates also the slightest momentary or permanent variations in the current or electromotive force.   The dead-beat quality is due entirely to the damping effect which the (copper or aluminium) frame of the coil experiences in moving through the strong magnetic field, the effect of friction in the bearings being practically naught owing to their construction and adjustment.

One of the most valuable features of the instrument is the uniformity of the scale.   All scale readings begin at zero, and it is hardly possible to discover with the naked eye any difference in the spacing of any two neighboring divisions.   Each individual instrument is carefully calibrated for a large number of readings, and the scale drawn according to these calibrated readings.   The divisions are drawn with extreme accuracy and

checked subsequently with the indications of a standard instrument.

Owing to the uniformity of the scale divisions, the fractions of a scale division may be estimated with great precision. As one-tenth of a scale division can be estimated easily, an apparatus ranging from 0 to 150 volts will allow reading to one-tenth of a volt. With the double-scale voltmeters, the lower scale of which ranges from 0 to 5 volts, one three hundredth of a volt may be read; and with the milli-voltmeters, the range of which extends from 0 to 0.01 volt on a scale divided into 100 divisions, readings may be taken which are accurate to one one hundred-thousandth of a volt. The same degree of accuracy is attained in the ammeters. Although the magnetic field in these instruments is produced by permanent magnets, experiment has shown that the magnetizing methods adopted render it constant, uniform, and not materially influenced by proximity to the powerful fields of dynamos.

Measuring the Electromotive Force of Batteries. — For measuring the E. M. F. of a single cell, the negative terminal (positive electrode) of the cell is connected to the rear binding post of the voltmeter at the left side, the positive terminal to the binding post at the right side. (See Fig. 6.) The readings then are taken on the lower scale.

Since this scale ranges from 0 to 5 volts, and is divided into 150 divisions, each division corresponds to $\frac{1}{30}$ of one volt, and since $\frac{1}{10}$ of a scale division may be distinctively estimated, the readings will be exact to $\frac{1}{300}$ of a volt.

If the pointer should be deflected to the wrong side, i.e., to the left, this would show that the poles of the cell have been connected with the binding posts the wrong way, and the connections must be exchanged.
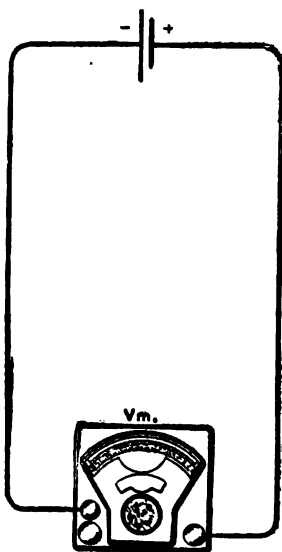

FIG. 6.—MEASURING THE E. M. F. OF A CELL.

If the E. M. F. of several cells arranged in series is to be measured, the negative (zinc) terminal is to be connected with the front binding post at the left hand (Fig. 7), and the deflection of the pointer is to be read on the upper scale. Since each division of this scale is equivalent to one volt, the readings will
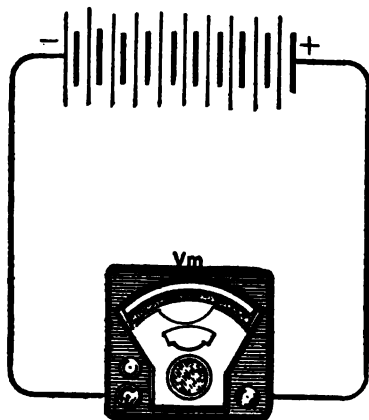
FIG. 7.—MEASURING THE E. M. F. OF A SERIES OF CELLS.

be correct to $\frac{1}{10}$ of a volt by estimating the tenth part of a scale division.

In case many measurements of E. M. F.'s are to be made in succession in a complicated system of conductors, in which the polarity of the current is not always known at the start, it is convenient to use an instrument provided with a reversing key. Turning the knob located behind the positive binding post by 90 degrees will reverse the direction of the current in the instrument, while turning it only 45 degrees will interrupt the current. When the needle is deflected the arrow marked on the head of the knob always points towards the binding post at which the current enters.

General Rules to be Observed in Using the Voltmeters.—A very valuable feature of the Weston voltmeters is their high internal resistance. The reason why this is of such great importance wherever measurements of differences of potential are to be made will be understood from the following:

If in Fig. 8 E is a current generator (dynamo, battery, etc.)

sending a current through the circuit AB while the voltmeter is not yet connected with the circuit, a certain difference of potential will exist between the points A and B. If then the terminals of the voltmeter are joined to the points A and B, a small part of the current will pass through the voltmeter, whereby the potential difference between A and B will be diminished slightly.
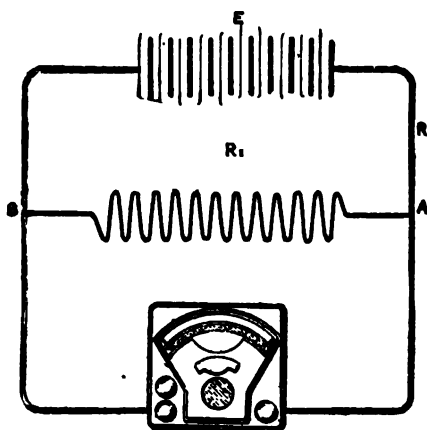
FIG. 8.—DIAGRAM TO ILLUSTRATE THE ADVANTAGE OF THE HIGH INTERNAL RESISTANCE OF THE WESTON VOLTMETER.

The difference of potential measured by the voltmeter is therefore not quite the same which existed between A and B before the voltmeter was connected. If, however, the resistance of the voltmeter is high, the variation is exceedingly small : the variation is smaller the greater the resistance of the voltmeter.

A short calculation and a few numerical examples will show clearly how exactly the accuracy of measurement is maintained in these voltmeters. For instance, let E, Fig. 8, be the E. M. F. of the generator ; R, the resistance of the generator and the parts AE and BE of the circuit ; R_1, the resistance AB. Then, if the voltmeter is not connected, the difference of potential between A and B is

$$e = \frac{R_1}{R + R_1} \times E.$$

If now the voltmeter is connected to A and B, the difference of potential between these points drops a little and becomes

$$e_1 = \frac{r \times R_1}{r \times R_1 + R \times R_1 + R \times r} \times E,$$

in which r is the resistance of the voltmeter. The difference between e and e_1 is

$$e - e_1 = \frac{1}{r} \times \frac{R_1 \times R}{R_1 + R} \times e_1,$$

and this expression will evidently be the smaller the greater r, the resistance of the voltmeter.

If, for instance, $E = 2$ volts, $R = 3$ ohms, $R_1 = 2$ ohms, and the resistance r of the voltmeter suitable for this case (0 to 5 volts) is 600 ohms, the error will be

$$e - e_1 = 0.0016 \text{ volt.}$$

If, however, an instrument had been used of only ten ohms resistance, the error would have been equal to 0.09 volt, or about 60 times as much as in the foregoing case.

The expression $\frac{R_1 \times R}{R_1 + R}$ represents the joint resistances of the parts AB and BEA of the circuit, if connected in multiple arc. We may therefore say that the error depends only on the proportion of this resistance to the resistance of the voltmeter.

If the measurement is to be correct to p per cent, the resistances R_1 and R must be chosen in such a way that $\frac{R_1 \times R}{R_1 + R}$ is smaller than $\frac{p \times r}{100}$ ohms.

If the circuit is not closed by a resistance R_1, the voltmeter is directly connected to the poles of E, and the value of e_1 becomes

$$e_1 = \frac{r}{r + R} \times E.$$

The error of measurement, or the difference between the value indicated by the voltmeter and the true value, is

$$E - e_1 = \frac{R}{r} \times e_1.$$

This error becomes smaller the larger the resistance of the voltmeter is in proportion to the internal resistance of the current generator.

If the measurement of the E. M. F. is to be correct to p per cent, the internal resistance R of the generator must be smaller than $\dfrac{p \times r}{100}$ ohms, in which r is the resistance of the voltmeter.

It will now be readily understood that the E. M. F. of cells of high internal resistance, as, for instance, that of Clark cells, cannot be determined by the method explained on page 39, not even with voltmeters of so high a resistance as that of the Weston instruments. If, for instance, the E. M. F. of a Clark cell is 1.438 volts and its internal resistance 1500 ohms, a voltmeter connected with the poles of the cell would show, not 1.438 volts, but only 0.41 volt.

The best and most exact way of determining the E. M. F. of such high-resistance cells is the Poggendorff-Clark method, explained on page 44.

Comparison of Electromotive Forces of Batteries.—(1) *Wheatstone's Method.*—Suppose the E. M. F.'s of two cells E_1 and E_2 are to be compared with each other (Fig. 9).

First connect E_1 in series with the voltmeter and a resistance R_1, and note the deflection V_1 of the pointer. Then increase the external resistance by an additional resistance r_1 and note the deflection V_2. Now join up the cell E_2 with such a resistance R_2 that the same deflection V_1 is obtained as before. Finally, increase R_2 by a resistance r_2 so as to make the deflection equal to V_2. Then

$$E_1 : E_2 = r_1 : r_2.$$

If E_1 is smaller than E_2, the resistance of the voltmeter itself may be taken as R_1. It is preferable to make r_1 about twice as large as the combined resistance of E_1 and R_1.

In this method it is not necessary that the internal resistances of the cells be small compared with the resistance of the voltmeter.

Example.—Let R_1 (the resistance of the voltmeter) be 600 ohms, and $V_1 = 1.45$ volts; let r_1 be 1200 ohms, and $V_2 = 0.48$ volt. If then, upon inserting E_2, an additional resistance of 36
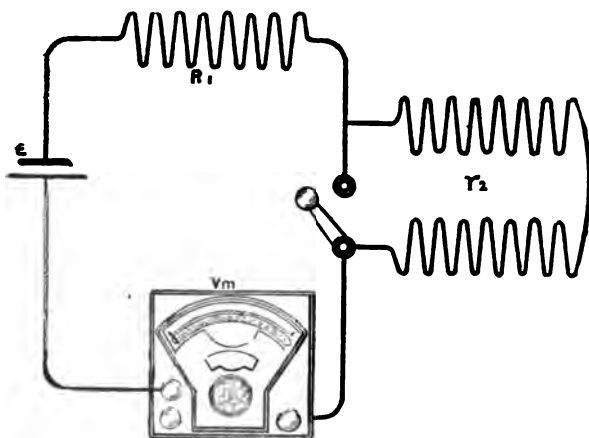
FIG. 9.—COMPARISON OF THE E. M. F.'S OF CELLS BY THE WESTON VOLTMETER.

ohms is required to make the deflection equal to 1.45 volts, and a resistance $r_2 = 1275$ ohms to produce the deflection of 0.48 volt, we shall have

$$E_1 : E_2 = 1200 : 1275;$$

therefore $E_2 = 1.062 E_1$, and $E_1 = 0.941 E_2$.

If the readings are correct to $\frac{1}{10}$ of a scale division, the error of measurement will be equal to about 1 per cent.

· (2) *Poggendorff's Method Modified by Clark.*—This method is very convenient for comparing the E. M. F. of any cell T, of low or high internal resistance, with that of a standard cell S (see Fig. 10).

B is a battery having a higher E. M. F. than either of the cells S and T to be compared. In series with B are connected a resistance R and a wire AD, along which a sliding contact may be moved. A millivoltmeter is connected with one pole to A, and the other to that pole of S which has the same polarity as the pole of B directly connected to A. The other pole of S is connected to the sliding contact, and is moved

to such a point C that the voltmeter points exactly to zero. Let r be the resistance of AC. The cell S is then disconnected, and the other cell T joined up in like manner to the millivolt-meter and the sliding contact. The latter is again brought to

such a point C_1 that no current is indicated by the millivolt-meter. Let the resistance of AC_1 be r_1. The proportion of the E. M. F.'s of S and T then will be

$$T : S = r_1 : r.$$

In practice it is most convenient to arrange the apparatus so that the value of T may be read directly in volts. To accomplish this, the wire AD is stretched over a suitably divided scale, the division starting at A. If now, for instance, S is a Clark cell having an E. M. F. of 1.44 volts, let the sliding contact connected to S be placed to division 144 and the resistance R be adjusted so as to bring the millivoltmeter to zero. After this adjustment is made, each of the divisions of the scale means $\frac{1}{100}$ of a volt. If, therefore, S is replaced by T, and if the sliding contact must be moved to division 175 in order to make the millivoltmeter point to zero, the E. M. F. of T is

equal to 1.75 volts. The accuracy of this method is exceed-
ingly high, if the resistance of S and T are only a few ohms.
In case the resistance of S is as high as in the usual Clark cell,
the accuracy amounts to about 0.4 per cent.

Measuring Current Strength with the Ammeter.—For meas-
uring the strength of the current the ammeter is generally used.
The instrument is to be inserted in the main circuit itself (see
Fig. 11), and the wires must be connected so that the current
from the positive terminal enters the upper one of the two bind-
ing posts situated at the right side of
the instrument. The needle then
is deflected to the right; a deflec-
tion to the left would show that the
connections have been made the
wrong way, and that the wires must
be exchanged. The pointer reads
directly in amperes.

This measurement of current
strength is exact to $\frac{1}{500}$ ampere if
an ammeter with a range from 0 to 5
amperes is used; and to $\frac{1}{10}$ ampere
if one with a range from 0 to 150 am-
peres is used. The limit of accuracy
of other ammeters is given by the
manufacturers.

It is often of importance that
the strength of the current should
not be altered essentially by insert-
ing an ammeter in the circuit.
Besides this, it is particularly im-
portant in station ammeters that
the instrument itself should absorb
as small a part as possible of the

FIG. 11.—MEASURING CURRENT
STRENGTH WITH THE AMMETER.

entire energy of the current, so as to avoid useless waste of
power. Both these requirements are fully met in the Weston
ammeters, in which the internal resistance is exceedingly small.

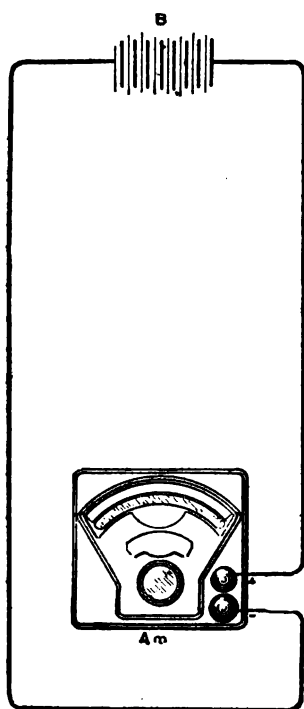Suppose, for instance, the very unfavorable case in which

150 amperes are flowing in a circuit of only 2 volts. The Weston ammeters then would absorb 4.95 watts, which is only 1.65 per cent of the entire energy of 300 watts.

In ordinary cases the resistance of the Weston ammeter may be neglected in comparison with the resistance of the rest of the circuit. Care should be taken, especially with strong currents, that the wires leading to the ammeter are of a proper size in order that they do not become overheated and do not introduce unnecessary resistance.

Measuring Current Strength with the Voltmeter.—If the resistance of a part of the circuit is known, or if the circumstances allow inserting a known resistance into the circuit, the strength of the current may be measured with a voltmeter.

In Fig. 8, let *R* be the known resistance between the points *B* and *C* of the circuit, and *A* the strength of the current to be measured. The binding posts of the voltmeter are connected to the ends *B* and *C* of *R*. If, then, the voltmeter indicates *V* volts, the intensity of the current in amperes is

$$A = \frac{V}{R}.$$

In this measurement it is advisable to pay attention to the following points: (1) That the wire of the resistance be thick enough to stand the current to be measured, without danger of being overheated or of having its resistance changed appreciably by the heat developed by the current. (2) The resistance introduced by the insertion of this wire in the circuit always reduces the current more or less; this must be taken into account in making accurate measurements.

If the reading is exact to $\frac{1}{m}$ volt, the measurement of current strength will be exact to $\frac{1}{m \times R}$ ampere. If, for instance, $R = \frac{1}{2}$ ohm and the readings are taken on a voltmeter ranging from 0 to 5 volts, then $\frac{1}{m}$ will be $\frac{1}{300}$ and the possible error will be

$$\frac{1}{m \times R} = \frac{2}{300} = \frac{1}{150} \text{amp.}$$

In this measurement it is most convenient to make $R = 1$ ohm. In this case the number of amperes measured is equal to the number of volts indicated by the voltmeter. If R be equal to $\frac{1}{10}$ ohm, the amperes of the current are equal to $\frac{V}{0.1}$, i.e., equal to the number of volts read, multiplied by 10. In general if $R = \frac{1}{n}$ ohm, the current is equal to $n . V$ amperes.

General Method of Measuring Resistances with the Voltmeter.—The resistance R to be measured is inserted in series with a current generator B (battery, dynamo, etc.), and with a known resistance R_1 (see Fig. 12). If now the voltmeter is

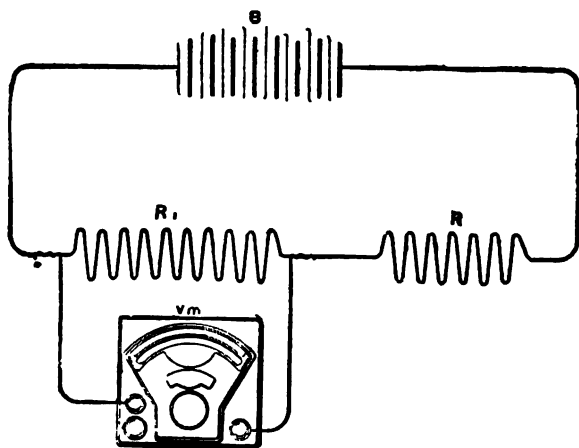FIG. 12.—METHOD OF MEASURING RESISTANCES WITH THE VOLTMETER.

connected to the ends of R_1, let the reading be V_1 volts, while if connected to the ends of R, let the reading be V volts; then

$$R : R_1 = V : V_1 ,$$

or

$$R = \frac{R_1 \times V}{V_1} \text{ ohms.}$$

If, for instance, $R_1 = 0.25$ ohm, $V_1 = 2.5$ volts, $V = 3.67$ volts, then

$$R = \frac{0.25 \times 3.67}{2.5} = 0.367 \text{ ohm.}$$

As mentioned before, the readings V and V_1, if taken on the lower scale of the ordinary double-scale voltmeter, are correct to $\frac{1}{300}$ volt. The error of a measurement of resistance will therefore be at the most equal to

$$100 \times \frac{1}{300} \left(\frac{1}{V} + \frac{1}{V_1} \right) \text{ per cent.}$$

In the last example the error would be equal to

$$\frac{1}{3} \times \left(\frac{1}{3.67} + \frac{1}{2.5} \right) = 0.2 \text{ per cent.}$$

If R_1 is very different from R, very small, for instance, compared with R, it is sometimes more convenient to measure V on the upper scale and V_1 on the lower one. The error then is at the most equal to

$$100 \times \left(\frac{1}{300 \times V_1} + \frac{1}{10 \times V} \right) \text{ per cent.}$$

If, for instance, $R_1 = 2.5$ ohms, $V_1 = 3.85$ volts (lower scale), and $V = 94.7$ volts (upper scale), then

$$R = \frac{2.5 \times 94.7}{3.85} = 61.5 \text{ ohms.}$$

The possible error would be

$$100 \times \left(\frac{1}{300 \times 3.85} + \frac{1}{10 \times 94.7} \right) = 0.19 \text{ per cent.}$$

This method may be modified by inserting an ammeter in place of the known resistance R_1, as shown in Fig. 13.

If, then, the ammeter reads A amperes, and the voltmeter reads V volts, the resistance R is calculated from the formula

$$R = \frac{V}{A} \text{ ohms.}$$

If, for instance, $V = 3.6$ volts, $A = 4.2$ amperes, then

$$R = \frac{3.6}{4.2} = 0.857 \text{ ohm.}$$

If an ammeter from o to 5 amperes, and a voltmeter from o to 5 volts, are used, the possible error would be

$$100 \times \left(\frac{1}{300 \times V} + \frac{1}{200 \times A} \right) \text{ per cent,}$$
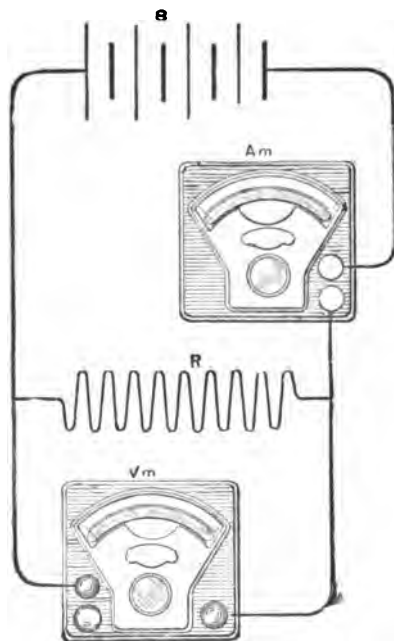
FIG. 13.—METHOD OF MEASURING RESISTANCES WITH THE VOLTMETER.

since the readings on the ammeter are correct to $\frac{1}{300}$ ampere, and those of the voltmeter to $\frac{1}{300}$ volt. In the foregoing example the error would be

$$100 \times \left(\frac{1}{300 \times 3.6} + \frac{1}{200 \times 4.2} \right) = 0.2 \text{ per cent.}$$

Measurement of Very Small Resistances.—A very valuable feature of the millivoltmeter is its adaptability for measuring small resistances. The method is the same as the one explained above (see Fig. 13).

The error caused by inaccurate reading is less the greater the current used. Consequently it is advantageous to make the current as large as the circumstances permit. On the other hand, the error will be larger the smaller the resistance to be measured.

If, for instance, the resistance of a certain length of a copper rod between the knife-edges B and C is to be measured, the connections are made as in Fig. 14. If the amperemeter
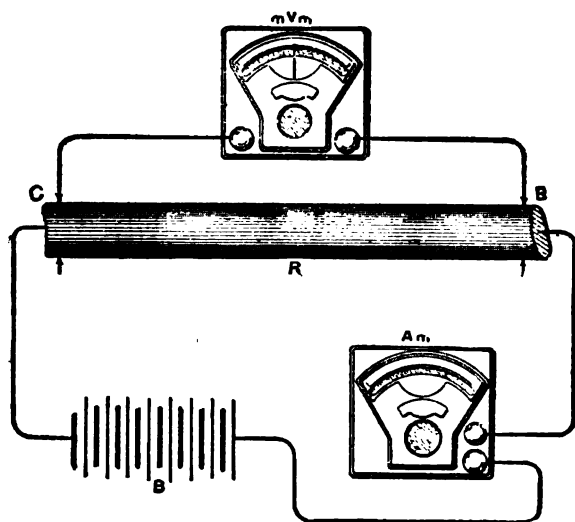
Fig. 14.—Measurement of Very Small Resistances.

indicates 35.4 amperes and the millivoltmeter 0.00875 volt, the resistance of the rod is equal to

$$R = \frac{V}{A} = \frac{0.00875}{35.4} = 0.000247 \text{ ohm.}$$

If an ammeter with a scale of from 0 to 50 amperes, and a millivoltmeter with a scale of from 0 to $\frac{1}{10}$ volt is used, and if the readings on both instruments are correct to $\frac{1}{10}$ of a scale division, the error of measurement is at the most equal to

$$100 \times \left(\frac{1}{100,000 \times 0.00875} + \frac{1}{20 \times 35.4} \right) = 0.25 \text{ per cent.}$$

The method explained in this paragraph for measuring low resistances with the millivoltmeter is preferable to that of the Wheatstone bridge, because the resistances of connection are eliminated in this method, while they may cause serious errors in the bridge method.

Measuring High Resistances.—High resistances are measured with the ordinary voltmeter, ranging from 0 to 150 volts, in the following way (Fig. 15):

Let r be the internal resistance of the voltmeter, and R the resistance to be measured. Connect the voltmeter to two
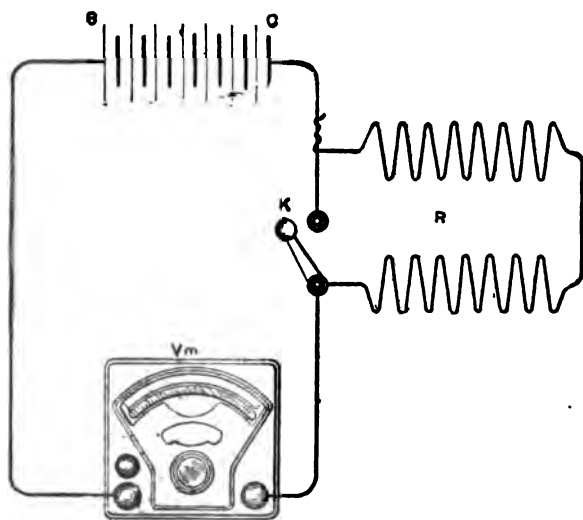
FIG. 15.—MEASURING HIGH RESISTANCES.

points B and C of a battery or source having as high a difference of potential as possible (not higher than 150 volts, of course), and read the deflection V of the pointer. Then insert the resistance R in circuit, which is most conveniently done by opening the key K. If, then, the deflection of the pointer is equal to V_1 volts, there will be

$$R = r\left(\frac{V}{V_1} - 1\right).$$

If, for instance, $V = 100$ volts, $V_1 = 40$ volts, and $r = 18,000$ ohms, then

$$R = 18,000\left(\frac{100}{40} - 1\right) = 27,000 \text{ ohms.}$$

If V and V_1 are exact to $\frac{1}{10}$ of a scale division, the error in the value of R will be at the most

$$\frac{10(V + V_1)}{V_1(V - V_1)} \text{ per cent.}$$

In the last example this error would be

$$\frac{10(100 + 40)}{40(100 - 40)} = 0.58 \text{ per cent.}$$

As a further calculation would show, the error will be a minimum for such resistances which are in the neighborhood of $1.4r$, that is, in the neighborhood of 25,000 ohms.

The following table shows the value of R that would correspond to a reading V_1 of the voltmeter, provided that the resistance r of the voltmeter be 18,000 ohms, and that the potential difference V be constantly equal to 100 volts. The column marked w shows the possible error of the measurement in percentage of R.

V_1	R (ohms).	w in %.	V_1	R (ohms.)	w in %.
95	900	4.1	9	192,000	1.33
90	2,000	2.1	8	207,000	1.47
80	4,500	1.1	7	240,000	1.64
70	7,700	0.8	6	281,000	1.89
60	12,000	0.67	5	342,000	2.21
50	18,000	0.60	4.5	382,000	2.43
45	22,000	0.58	4.0	432,000	2.71
40	27,000	0.58	3.5	497,000	3.0
35	33,500	0.59	3.0	582,000	3.5
30	42,000	0.62	2.5	703,000	4.2
25	54,000	0.67	2.0	892,000	5.2
20	72,000	0.75	1.5	1,182,900	6.8
15	102,000	0.90	1.0	1,780,000	10.2
10	162,000	1.22			

Measuring the Internal Resistance of Batteries. *First Method.*—In Fig. 16 E is the battery or single cell to be measured ; K is an interrupting key, and R a suitable resistance.

If K is open, the voltmeter (ranging from o to 5 volts) indicates the E. M. F. of the cell, which is, say, E volts. Upon pressing down the key K, the voltmeter reads the potential difference e existing between the ends of R. Then the internal resistance r_1 of the cell is equal to

$$r_1 = R \times \frac{E - e}{e} \text{ ohms.}$$

If, for instance, $E = 1.5$ volts, $e = 1.35$ volts, and $R = 4$ ohms, then

$$r_1 = 4 \times \frac{1.5 - 1.35}{1.35} = 0.44 \text{ ohm.}$$

The accuracy of this measurement is not much higher than about five per cent, but for the internal resistance of cells this degree of accuracy is sufficient in most cases.
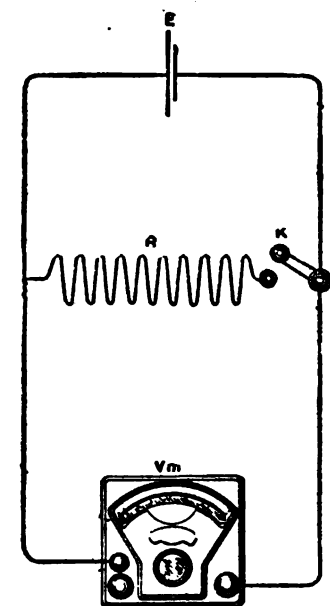
FIG. 16.—MEASUREMENT OF THE INTERNAL RESISTANCE OF CELLS.

It may be mentioned here that the internal resistance as well as the E. M. F. of cells is not a constant quantity, but depends upon the strength of the current passing through the cell. This current, which is equal to $\frac{e}{R}$, may be regulated as required by adjusting R. In the example mentioned it is $\frac{1.35}{4} = .34$ ampere. The key K is generally kept closed, and is opened only as long as is necessary to measure the value of E.

Second Method (Siemens-Froelich).—The cell E to be measured is joined up with the resistance R_1 R_2 and r_1, as illustrated in Fig. 17. By means of the key K the point A may be connected either with B or with C. If A is connected to C, r_1 is a shunt to R_1, while upon connecting A to B the resistance R_2 and r_1 is a shunt to R_1. The voltmeter (0–5 volts) is connected to the terminals of r_1 in both cases.

Now, the value of r_1 is adjusted in such a way that the deflection V of the voltmeter remains unaltered whether A be connected to B or to C. Then the resistance of the element E will be exactly equal to r_1.

It is advisable to connect an auxiliary known resistance r_2 in series with E for the proper regulation of the current
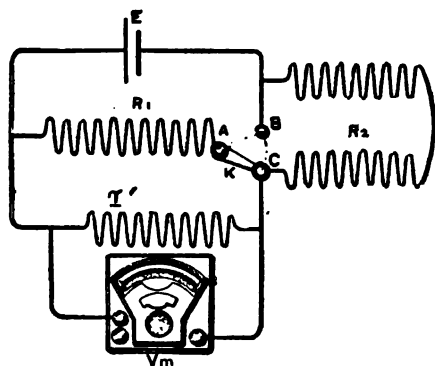
FIG. 17.—MEASUREMENT OF THE INTERNAL RESISTANCE OF CELLS.

strength; this must be deducted from the value of r_1. If the resistance of the cell is known approximately, it is best to make R_2 equal to about one and a half times the sum of r_2 and the internal resistance of the element, and to make $R_1 = \frac{1}{2}R_2$.

The following example will illustrate the method. If it is known that the resistance of the cell is about 1 ohm, then make $r_2 = 5$ ohms.

$$R_2 = 1.5(1 + 5) = 9 \text{ ohms.}$$
$$R_1 = \tfrac{1}{2}R_2 = 4.5 \text{ ohms.}$$

If, then, r_1 must be made equal to 6.2 ohms in order to obtain no variation of the deflection of the voltmeter upon interchanging the connection of A with B and C, the resistance of the cell will be

$$6.2 - 5 = 1.2 \text{ ohms.}$$

An error of $\frac{1}{10}$ of a scale division will produce an error of about 0.5 per cent in the value of r_1.

Half-Deflection Method.—The cell or battery, the unknown resistance of which may be R ohms, is joined up in series with a millivoltmeter ranging, for instance, from 0–0.04 volt and
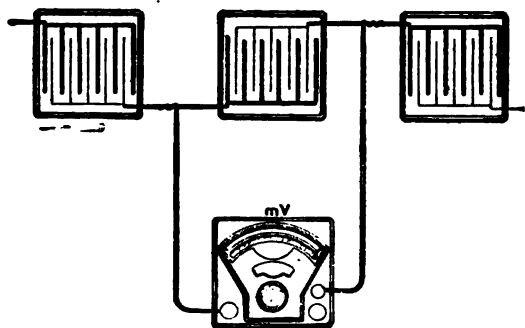
with a suitable resistance R_1 of such an amount as to produce nearly the whole scale deflection. Then the resistance R_1 is increased to R_2 ohms, so that exactly half the former deflection is obtained. Then there will be, if r is the resistance of the millivoltmeter,

$$R = R_2 - (2R_1 + r) \text{ ohms.}$$

If, for instance, $r = 1$ ohm, $R_1 = 16.25$ ohms, $R_2 = 35.5$ ohms, then $R = 35.5 - (35.5 + 1) = 2$ ohms.

As the polarization of a cell depends on the strength of the current flowing through the cell, a certain error is caused by this fact in this method, and this error is much higher than the one caused by the admissible error in the readings of the millivoltmeter. Nevertheless, this method is accurate enough for practical work.

Testing Accumulators.—The voltmeter is particularly well adapted for accumulator work, especially for the examination of the single cells.

The examination of the single cells, which ought to be made at least twice a week, has heretofore been made by
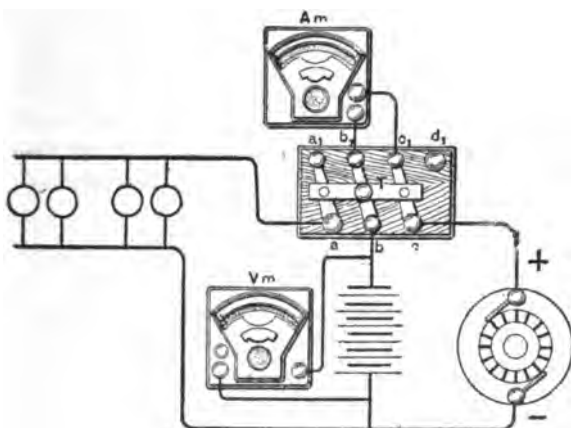
Fig. 19.—Arrangement of Apparatus for Testing Accumulators.

means of a small 2-volt incandescent lamp attached to the cell terminals, the degree of brightness of this lamp being taken as an indication of the state of the cell. It is unnecessary to say how poor a method this is. If, however, the Weston voltmeter, which is just as convenient (ranging from o to 5 volts), be used, instead of the incandescent lamp, the voltage is read directly to fractions of $\frac{1}{100}$ of a volt.

In charging a secondary battery it is an important point, as is well known, not to exceed a certain maximum charge, because otherwise the battery will be damaged and most of the current wasted, more than 90 per cent of it being consumed in developing oxy-hydrogen gas. Of the methods for ascertaining the limit of charge, as, for instance, watching the development of gas-bubbles, the density of the acids, etc., none is as accurate as or more convenient than the observation of the pressure at the terminals by means of the voltmeter. The charging is

continued until the voltmeter indicates the maximum pressure allowed for the battery (ordinarily about 2.5 volts per cell) and is then stopped. On discharging, also, it is certainly more reasonable to determine the limit of the discharge from the indications of the voltmeter than from the decrease of brightness of the incandescent lamps. The discharging is stopped when the voltmeter reads 1.85 or 1.80 volts per cell, according to the requirements made by the makers.

The charging as well as the discharging current is measured by means of an ammeter. At the beginning of the discharge the connections with the ammeter must be reversed, the direction of the current being reversed, while no change is required for the connections of the voltmeter.

It is convenient to arrange the apparatus as shown in Fig. 19. For charging the switch T is turned so as to connect b_1 to b and c_1 to c. For discharging the switch is moved so as to connect a to b_1 and b to c_1. The ammeter connected to b and c_1 is then always properly connected.

In case a single accumulator cell is to be tested more particularly, all measurements (electromotive force, internal resistance, voltage at terminals, etc.) may be carried out with one voltmeter (0 to 5 volts) by using the following arrangement (Fig. 20).
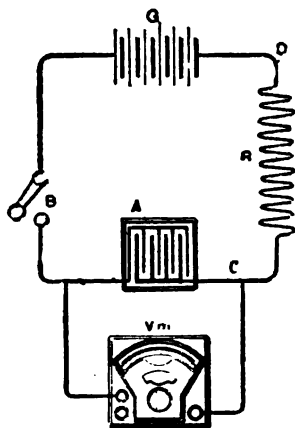
Let A be the accumulator to be charged from the current generator G, R a resistance of one ohm; for instance, if the circuit is closed at B and the voltmeter attached to B and C as shown, then the voltmeter will give the voltage e at the terminals of the accumulator A while charging.

FIG. 20.—ARRANGEMENT OF APPARATUS FOR TESTING ACCUMULATORS.

By shifting the connections of the voltmeter to C and D, the strength C of the current passing through A is found; and if the voltmeter is connected again to B and C after opening the key at

B, the voltmeter indicates the electromotive force E of the accumulator.

If r_1 is the internal resistance of the accumulator, then during the charge

$$e = E + r_1 \times C, \quad \text{or} \quad r_1 = \frac{e - E}{C}.$$

During the discharge through a resistance R_1 (Fig. 21) the measurement is the same, but then

$$e = E - r_1 \times C,$$

or

$$r_1 = \frac{E - e}{C}.$$

If, for instance, during the charge $e = 2.35$ volts, $E = 2.20$ volts and $C = 5$ amperes, then
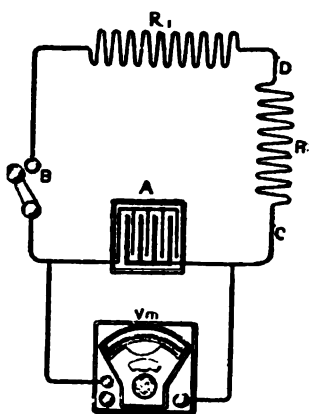
FIG. 21.—ARRANGEMENT OF APPARATUS FOR TESTING ACCUMULATORS.

$$r_1 = \frac{2.35 - 2.20}{5} = \frac{0.15}{5} = 0.03 \text{ ohm.}$$

Precautions to be Observed in Using the Weston Instruments.—As mentioned before, it is advisable to avoid violent shaking of the instruments, since the pivots and jewelled bearings of the movable coil might thereby be damaged.

The influence of magnetic fields upon the instruments is objectionable only if the fields are very strong and if the instrument happens to come into close proximity with them. A Weston shunt dynamo of medium size running with a voltage of 130 volts hardly affected the readings at a distance of three feet, while at a distance of five feet no effect whatever could be noticed. To be perfectly safe, it is advisable not to place the instrument in the immediate neighborhood of dynamos or heavy currents on switch-boards.

The instrument should be placed *approximately horizontal* when measurements are to be made. In case a small inclina-

tion is desirable, this inclination should never be so large that the pointer deviates from the zero point when the instrument is not in circuit.   If the instrument is used at an inclination, the friction in the bearings may be slightly increased, thus impairing the accuracy of the indications.   Large masses of iron should be avoided in close proximity to the instrument, and it should never be placed on top of a dynamo, running or idle, on steam-chests, steam-pipes, iron steam-radiators, bus-bars, etc.   Anything of that kind will not affect the magnet permanently, but it will change the reading of the instrument for the time being.   Neither should the instrument be put in a hot place, since this might melt off the paraffine insulation on the resistance-coil.   If the instrument is to be fastened down, brass screws should be used, and not iron nails or spikes (all cases which come within the actual experience of the manufacturers).

In making connections for the voltmeter, thin flexible wire, well insulated, should always be used, and proper care taken that no short circuit is made through the metal case (an accident happening rather often through carelessness of the user) by touching it with the bare ends of the two pressure wires.

Wiping the glass cover before making a reading should be avoided.   Neglect of this rule frequently causes great discrepancies in the readings of electrical measuring instruments ; the very light aluminium pointer of the instrument being affected by the static charge of the glass, electrified by wiping with a dry cloth or chamois-skin.

Finally, it is scarcely necessary to mention that to exceed the upper limit of current or voltage for which the instruments are constructed would be highly objectionable and must be strictly avoided.

Standardizing the Weston Voltmeters.—If a suspicion arises that the apparatus has been injured by some accident, and if another Weston voltmeter is available, the simplest way of checking the indications, of course, would be to connect the two instruments in multiple arc and to compare their readings.

In case the scales of the two instruments are different, they may still be compared, if a suitable resistance be connected in series, with the instrument designed for the lower voltages, so as to make the sensitiveness of both instruments alike.

A voltmeter supplied with a calibrating coil may be checked very easily by connecting it with the poles of a cell of known and constant E. M. F. (Daniell cell, Callaud cell, etc.). If the deflection produced by such E. M. F. has once been noted, it is evident that it may be used as a check for all future occasions. Elements of a very high resistance (as Clark's cells and similar standard cells) must not be used for this purpose on account of their rapid polarization even when made to give a very small current.

If a more accurate calibration is desired, independent of the indications of other instruments, a modification of the methods explained may advantageously be applied in the following way:

Suppose the range of the voltmeter to be from 0 to 150 volts. Let B (Fig. 22) be a current generator of constant
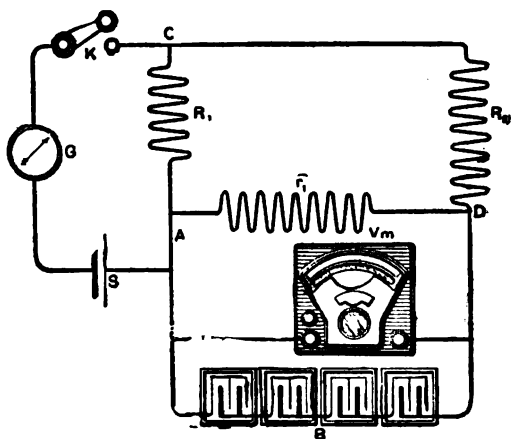
FIG. 22.—STANDARDIZING THE WESTON VOLTMETERS.

E. M. F., capable of producing between A and D a potential difference E up to 150 volts. Let r_1 be a resistance serving to

regulate the actual amount of potential difference between A and D. To these points are connected the terminals of the voltmeter, as well as a shunt containing the resistances R_1 and R_2. Another shunt containing a standard cell S of known E. M. F., a mirror or other sensitive galvanometer G, and a key K are connected to the ends A and C of the resistance R_1. The pole of the standard cell connected to A must be of the same polarity as the pole of B, which is connected to A.

The resistances R_1 and R_2 must now be adjusted in such a way that, upon closing K, no deflection of G is obtained. When this is the case, the proportion between the electromotive forces E and S will be $E : S = R_1 + R_2 : R_1$, or

$$E = \frac{R_1 + R_2}{R_1} \times S.$$

For instance, let S be a Clark cell having at the existing temperature an E. M. F. of 1.45 volts. Let $R_1 = 145$ ohms and $R_2 = 9737$ ohms be the resistances with which no deflection was obtained in the galvanometer G. Then

$$E = \frac{9737 + 145}{.145} \times 1.45 = 98.82 \text{ volts.}$$

It is most convenient to make $R_1 = 100 \times S$ ohms, S being the number of volts of the standard cell, and to bring the current passing through G to zero by properly adjusting the value of R_2. In that case

$$E = 0.01 \ (R_1 + R_2) \text{ volts.}$$

Standardizing the Weston Ammeters.—The most obvious way of checking a Weston ammeter, of course, is to compare it with a similar and reliable instrument, if available, by joining up the two instruments in series.

As with the voltmeters, the instruments need not necessarily be constructed for the same range of current. It suffices to properly reduce the sensitiveness of the ammeter designed for lower currents by applying a shunt of suitable resistance.

Since current strengths may also be measured with the

voltmeter, an ammeter may also be standardized by means of a reliable voltmeter. The terminals of the voltmeter are then connected to the terminals of a suitable and known resistance inserted in the circuit of the ammeter. The calibration can then be readily accomplished.

Of course the same method could serve inversely to calibrate a voltmeter by means of a reliable ammeter.

Another reliable way of calibrating an ammeter, independently of the indications of other instruments, is to connect it up in series with a constant current generator B and a copper or silver voltameter (see Fig. 23). The cathode K, that is, the
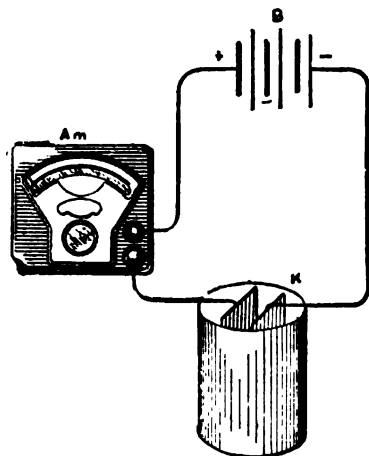
FIG. 23.—STANDARDIZING THE WESTON AMMETER.

plate on which the metal is deposited, is to be connected with the negative terminal of B. Since a current of one ampere passing for one minute deposits 0.304 grain of copper and 1.035 grains of silver, the strength C of the current used may easily be determined by the increase M in weight of the cathode. If M is also measured in grains, and if the current was passing through the voltameter during t minutes, then (see page 72)

$$C = \frac{M}{c \times t} \text{ amperes.}$$

C being 0.304 if the copper voltameter, and 1.035 if the silver voltameter is used.

If, for example, $M = 7.25$ grains, $t = 30$ minutes, there will be, in case of a copper voltameter,

$$C = \frac{7.25}{0.304 \times 30} = 0.794 \text{ ampere.}$$

GROUPING OF CELLS.

The cells forming a battery may be arranged—

1. In series (sometimes termed " in tension " or " tandem "),
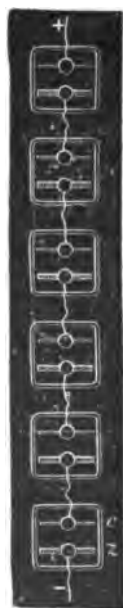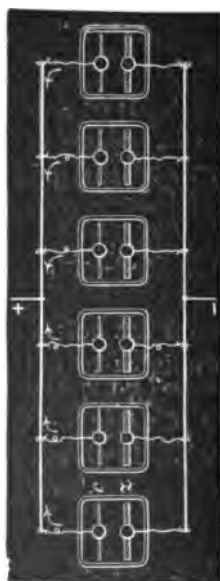
FIG. 24.   FIG. 25.

the positive terminal of one cell being connected to the negative of the next and so on successively (Fig. 24).

2. In multiple arc (sometimes termed " in parallel," " in sur-

face," "in derivation," and "in quantity"), in which the like-named terminals are united (Fig. 25).

3. In mixed relation, in which the cells are arranged in several groups united in series, each group being composed of several members united in multiple arc (Fig. 26).

1. *Grouping in Series.*—According to Ohm's law,

$$C = \frac{nE}{nR + r}$$

in which E = E. M. F. of each cell of the battery;

R = internal resistance;

r = external resistance (circuit);

n = number of cells forming the battery.

In applying the formula it is often possible to neglect either R or r. R or even nR being negligible as compared with r, the current from a single cell will be $C = \dfrac{E}{r}$ (approx.), and for n cells $C = \dfrac{nE}{r}$ (approx.).

FIG. 26.

If, on the other hand, r is negligible as compared to R, the current from a single cell will be $C = \dfrac{E}{R}$, and for n cells $C = \dfrac{nE}{nR} = \dfrac{E}{R}$. It is important to note that n cells in series offer n times the resistance of one cell—since in the former the length l of the liquid column traversed is n times that in the latter.

2. *Grouping in Multiple Arc.*—Ohm's law gives

$$C = \frac{E}{\dfrac{R}{n} + r}.$$
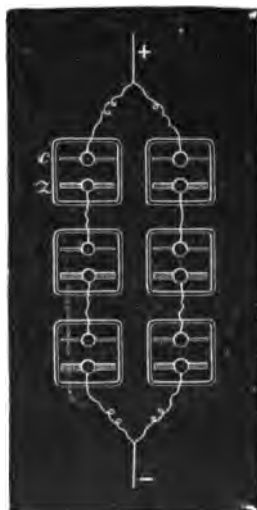
Neglecting R, we have $C = \dfrac{E}{r}$ (approx.), which obviously gives no advantage over the single cell. Neglecting r, we have $C = \dfrac{E}{\dfrac{R}{n}} = \dfrac{nE}{R}$ (approx.), whence it results that the current increases proportionately to the number of cells, and decreases nearly proportionately to the resistance.

3. *Mixed Grouping.*—Grouping in series and grouping in multiple arc may be combined so as to arrange a battery so as to yield a maximum current. Thus if we have a battery of n cells, each of E. M. F. E, and of internal resistance R, it is of great importance to arrange them so as to drive the largest possible current through a given external resistance r.

If n has factors m and l, we may couple the cells so as to have m in series and l parallel. We thus get a battery of E. M. F. $= mE$, and of internal resistance $= \dfrac{mR}{l}$. The current obtained will be

$$C = \frac{mE}{\dfrac{mR}{l} + r}.$$

If we investigate, either algebraically or by means of the calculus, the arrangement that will give a maximum value of C, we find that this occurs when

$$\frac{m}{l}R = r.$$

Or, *we obtain the maximum current with a given battery when it is so arranged as to make the internal resistance as nearly as possible equal to the external resistance.*

It is therefore convenient to have a battery in which the number of cells is a number having several pairs of factors.

Example (Larden).—We will here assume current, E. M. F., and resistance to be expressed in the units *amperes*, *volts*, and *ohms*, respectively.

Let us have $n = 24$, $E = 2$ *volts*, $R = 2$ *ohms*, and $r = 3$ *ohms*.

Then we have the following arrangements possible:

(i) 24 *cells end-on.*

    Here $C_1 = \dfrac{24 \times 2}{24 \times 2 + 3} = \dfrac{48}{51} = \dfrac{16}{17}$ *amperes.*

(ii) 12 *cells end-on, 2 parallel*

    Here $C_2 = \dfrac{12 \times 2}{\frac{12}{2} \times 2 + 3} = \dfrac{24}{15} = \dfrac{8}{5}$ *amperes.*

(iii) 8 *cells end-on, 3 parallel.*

    Here $C_3 = \dfrac{8 \times 2}{\frac{8}{3} \times 2 + 3} = \dfrac{16}{\frac{25}{3}} = \dfrac{48}{25}$ *amperes.*

(iv) 6 *cells end-on, 4 parallel.*

    Here $C_4 = \dfrac{6 \times 2}{\frac{6}{4} \times 2 + 3} = \dfrac{12}{6} = 2$ *amperes.*

(v) 4 *cells end-on, 6 parallel.*

    Here $C_5 = \dfrac{4 \times 2}{\frac{4}{6} \times 2 + 3} = \dfrac{8}{\frac{13}{3}} = \dfrac{24}{13}$ *amperes.*

It is needless to contiuue, for it is clear that (iv) gives us the greatest current. And Case (iv) is that in which the internal resistance of the battery is 3 ohms, or equals the external resistance. Of course, we cannot in general so subdivide our battery as to make the equality exact.

STANDARD CELLS.

Although no absolute standard of the unit of electromotive force (the volt) exists, yet there are several standards of known value with which comparisons can be made. The cells most generally employed as standards are some form of Daniell gravity cell, in which the copper sulphate and the zinc sulphate solutions mix very slowly, or the form of cell

commonly known as "Latimer Clark's." The latest type of standard cell is that devised by Mr. Edward Weston. These cells will be found described in their proper classifications under the following heads: Ayrton and Perry, Reynier, London Post Office, Kittler, Lodge, Latimer Clark, Warren De la Rue, Regnault, Weston, and Carhart.

In measuring the E. M. F. of a battery it is compared with a standard of one or more cells, and, the relative values of the two being determined, the E. M. F. of the battery in volts is obtained by ordinary proportion. For example, the relative E. M. F.'s of a battery and three standard Daniell cells was found to be as 1.25 to 1. The E. M. F. in volts of the battery was therefore

$$1.25 : 1 :: 3 \times 1.079 : x,$$

or

$$x = \frac{1 \times 3 \times 1.079}{1.25} = 2.59 \text{ volts.}$$

THE VOLTAMETER.

This apparatus, which is employed to measure current strength, usually consists of a glass vessel filled with acidulated water in which are plunged two wires or plates of platinum which serve to transmit the current whereby the water is decomposed. In Fig. 27, V is the vessel containing the acidulated water; L L', platinum electrodes respectively connected to the binding posts A and B, and placed in the inverted test-tubes H O. The gases evolved accumulate in the upper portions of the test-tubes. In the form of apparatus represented in Fig. 28 the test-tubes C C', which are arranged in the vessel B and which receive the platinum electrodes P P', are graduated, so as to allow of convenient measurement of the accumulated gases. At their upper portion the tubes are greatly reduced in diameter (T T') and provided with stop-cocks R R'—an arrangement which allows of the electrolyte

being drawn out the tubes by aspiration and which therefore
obviates the need of displacing the tubes in order to fill them.
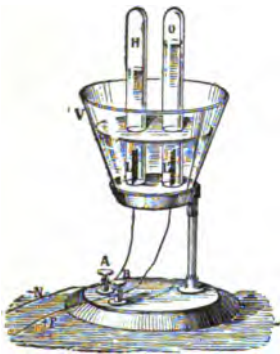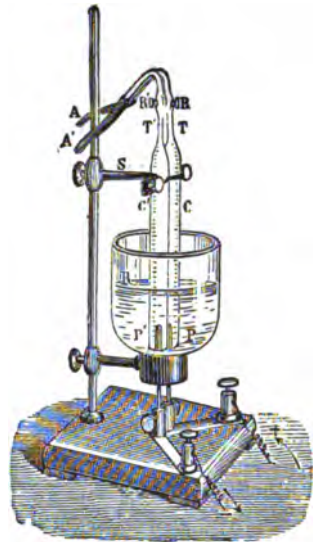
FIG. 27.   FIG. 28.
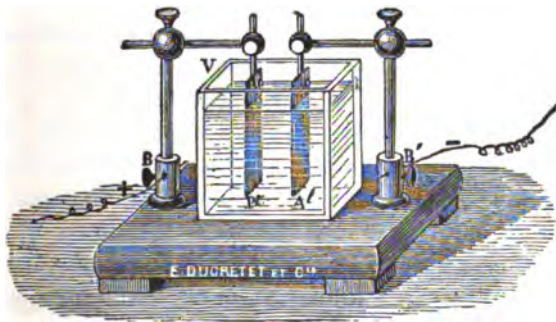
FIG. 29

The voltameter most commonly employed is that in which
the electrolyte is a solution of sulphate of copper, the con-
struction being as shown in Fig. 29.

The sulphate of copper solution should be chemically pure.

According to the experiments of Soret, however, the quantity of metal precipitated will be always very nearly the same whatever may be the nature of the solution.   Thus he finds as the weight of copper precipitated by one ampere of current during one hour, the following:

Sulphate of copper at saturation...........	1.1812	grams.
" " " diluted with 1 vol. of water	1.1835	"
Nitrate of copper, concentrated...........	1.1805	"
Phosphate of copper dissolved in phosphoric acid..	1.1800	"
Acetate of copper..:......................	1.1799	"
Mixture of sulphate of copper and sulphate of potassium...........................	1.1806	"
Mixture of sulphate of copper and nitrate of cobalt....................................	1.1825	"
Mixture of sulphate of copper and sulphate of zinc....................................	1.1835	"
Mixture of sulphate of copper and sulphate of cadmium................................	1.1835	"

According to V. Dupré (1857), when certain of the salts of copper with organic acids are electrolyzed the resulting deposit is sometimes brown and sometimes bright red and its weight is greater than that of the copper deposited in the sulphate of copper voltameter.   This coloration of the deposit, as well as the augmentation of its weight, is due to the formation of copper oxide.   The production of this compound ceases on operating in a vacuum if a concentrated solution and an energetic current be employed, or even if the solution is acid.   The best way of avoiding the formation of the oxide is to work with concentrated solutions and a strong current.

The sulphate of copper solution is best composed of a mixture of 3 parts of cold saturated sulphate solution with 2 parts of distilled water.   If the solution is too dilute, a portion of the sulphuric acid will remain therein and will not combine with the anode.   It is advantageous to agitate the solution

before each test with pure cupric hydrate recently precipitated.

The copper anode should be in the form of a plate and should have a surface (one side) of 5 square decimeters plunged in the liquid. A platinum anode will not give absolutely exact results. Ponthière states as follows: If there be interposed in the circuit and in tension two sulphate of copper voltameters, one of which has copper and the other platinum electrodes, it will become plainly apparent by repeated weighings that after a certain period of operation the weights of the two copper deposits are no longer equal per given time. The solution of the second voltameter becomes more and more impoverished of copper and enriched with sulphuric acid. The latter becomes partly electrolyzed and the energy expended by the current in the second voltameter is distributed in reality between two different electrolytes.

In the sulphate of copper voltameter the cathode should be a plate of platinum having a surface a little larger than that of the copper anode. Before using the platinum plate it should be placed for some time in dilute boiling nitric acid, then carefully washed in distilled water and dried between leaves of filtering-paper. Finally it may be passed through the non-luminous flame of the Bunsen burner, cooled and weighed.

The strength of current should not exceed from 2.5 to 3 amperes per square decimeter of cathode. The temperature of the solution should not be above 40°C.; otherwise there will be notable oxidation of the copper. Not less than 1 gram of copper should be deposited in order that slight errors in weight may not materially influence the result.

When the voltametric test is terminated, the plate is removed quickly from the solution, washed in distilled water, dried between leaves of filtering-paper and left standing on end for several hours. The quantity Q in coulombs which has traversed the voltameter is calculated from the electro-chemical equivalents. The strength of current C may be obtained by the formula

$$C = \frac{Q}{t} \text{ amperes,}$$

in whfch *t* represents the time in seconds during which the current has passed. For convenience, however, it may be noted that one ampere of current deposits 0.00111815 gram or 0.017253 grain of silver per second on one of the plates of a silver voltameter, the liquid used being a 15 to 30 p. c. sol. of silver nitrate ; 0.00032959 gram or 0.005084 grain of copper per second on one of the plates of a copper voltameter, and 0.0003392 gram or 0.005232 grain of zinc per second on one of the plates of a zinc voltameter, and also to decompose 0.00009326 gram or 0.001439 grain of dilute sulphuric acid per second. Hence, if $C = $ current strength in amperes, $M = $ amount of metal deposited or sulphuric acid decomposed in given time, $c = $ amount of metal deposited or sulphuric acid decomposed by 1 ampere, and $t = $ time in seconds, we have, as expressing the relation of the factors, $C = \dfrac{M}{c \times t}$ (see page 63).

In order to determine small quantities of copper it is preferable to use as electrodes very fine and short copper wires instead of plates of that metal. Lenz has constructed a very accurate voltameter in which there is measured the volume of mercury set at liberty during electrolysis of mercurous nitrate. The calculation is the same as for copper.

THE POSSIBILITIES AND LIMITATIONS OF CHEMICAL GENERATORS OF ELECTRICITY.[*]

The electromotive force which a given battery or combination of materials will develop is the first and most important question in electro-chemistry. Of course the best and surest way to arrive at this E. M. F. is to determine it by actual experiment with a voltmeter, or, still better, by comparison with a standard cell. There are, however, many times when the materials or instruments are not at hand, and a calculation or predetermination of the E. M. F. is very convenient.

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[*] From a paper by Prof. F. B. Crocker read before the American Institute of Electrical Engineers, 1888.

The formula for calculating the E. M. F. is obtained by assuming that the electrical energy of the given chemical combination is equal to the heat energy which the same combination is capable of producing, or $EC = 4.16CaH$. That is, volts multiplied by coulombs is equal to the coulombs multiplied by the electro-chemical equivalent, i.e., the weight of material required per coulomb and that by the heat produced by one gram of the material. Cancelling the C in both members, we have $E = 4.16aH$, in which E is the E. M. F. in volts, a is the electro-chemical equivalent (grams per coulomb), and H is the number of heat units (gram-degrees Cent.) produced per gram of material by the given chemical combination. The values of a and H are given for most materials in electrical and chemical books of reference, and the calculation is a very simple one. Nevertheless this formula and the principle involved in it are not generally understood and are very seldom used. The equation deduced above is that ordinarily given, but what has been found to be a more convenient form of it is obtained by assuming that $E = H$, giving a its value for hydrogen (.00001035). Solving with respect to H we have $H = 23,300$, which means that 23,300 is the number of heat units per equivalent corresponding to one volt,* and all that is necessary to find the E. M. F. of any given chemical combination is to divide the number of heat units per equivalent (which is the form they are almost always given in) by 23,300 and the quotient is the E. M. F. in volts. For example, to obtain the E. M. F. which zinc and free chlorine will develop divide 48,600 (which is the number of heat units produced by the combination of one equivalent of zinc with one of chlorine as given by Thomsen) by 23,300, and the result 2.09 is certainly very close to 2.11, the actual value obtained by experiment. In the same way the E. M. F. of other combinations of materials may be predetermined, but it should always be borne in mind that the heat of combination corresponding to one *equivalent* of the material should be taken and not necessarily that corresponding to one atom ; as, for example, in the case of zinc, the heat per atom (65 grams) is 97,200, which has to

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* See note, page 86.

be divided by 2 to reduce it to one equivalent, because zinc is a dyad and takes two atoms of chlorine, which is a monad. In the case of monad metals like sodium, potassium, and silver the figures may be taken just as they are given in the tables. Mistakes very frequently arise in this way; in fact, there is seldom found a table of electro-chemical equivalents in which this point was correctly introduced in every case.

In order to test the practicability and accuracy of calculating E. M. F., as well as to obtain reliable results and full data for their own value, the E. M. F. given by thirteen of the most important metals was determined in combination with free chlorine, bromine, and iodine, and the results are given in Tables A, B, and C, respectively. In Table D these results have been averaged and placed side by side with the results obtained by calculation. The agreement between the two sets of figures is not perfect by any means, but when it is remembered how the E. M. F. of a cell will change one or two tenths of a volt on apparently the slightest provocation, it will be evident that the figures are strikingly close. In more than half of the cases the difference is less than one-tenth of a volt, and the average difference is only slightly more than that.

TABLE A.

E. M. F. produced by different metals in combination with free chlorine in solutions of—

Metals.	Magnesium Chloride.	Zinc Chloride.	Zinc Chloride.	Zinc Chloride.	Hydro-chloric Acid.	Common Salt.	Aver-age.
Magesium....	2.83 2.65	2.65			3.2–3.15	2.85	3.1
Zinc..........	2	2.20	2.13	2.11	2.20	2.18	2.11
Cadmium.....		1.94		1.86	1.98	1.93	1.9
Aluminium...	1.75	2.04	1.88		1.02	1.98	2
Iron..........		1.60	1.56	1.5	1.67	1.68	1.6
Cobalt........		1.43	1.43	1.41	1.50	1.45	1.43
Nickel.......		1.33		1.27	1.40	1.33	1.33
Tin..........	1.50	1.70	1.6	1.57	1.68	1 66	1.61
Lead.........		1.63	1.62	1.60	1.68	1.65	1.63
Copper.......		1.31	1.30	1.29	1.37	1.34	1.32
Silver........		1.11	1.12	1.13	1.15	1.10	1.11
Antimony....		1.20	1.23	1.25	1.25	1.08	1.22
Bismuth......		1.29	1.25	1.20	1.27	1.19	1.21

TABLE B.

E. M. F. of different metals with free bromine in solutions of

Metals.	Magnesium Bromide.	Nickel Bromide.	Potassium Bromide.	Hydro-bromic Acid.	Magnes. Bromide weak.	Average.
Magnesium.....	2.55	2.45	2.51	2.7	2.57	2.56
Zinc...........	1.84	1.78	1.82	1.79	1.85	1.79
Cadmium	1.6	1.54	1.62	1.57	1.61	1.58
Aluminium.....	1.5	1.46	1.47	1.46	1.6	1.53
Iron...........	1.22	1.25	1.31	1.26	1.33	1.3
Cobalt.........	1.1	1.02	1.05	1.06	1.13	1.05
Nickel.........	.8	.85-.8	.8	.87	.94	.85
Tin............	1.12	1.31	1.3	1.25	1.27	1.3
Lead..........	1.4	1.27	1.33	1.28		1.33
Copper	1.05	.96	1.01	.99	1.03	1.02
Silver.	.97	.94	.97	.95	.93	.95
Antimony......	.99	.73	.71	.87	.97	.8
Bismuth.......	.92	.9	.96	.88	.92	.92

TABLE C.

E. M. F. of different metals with free iodine in solutions of

Metals.	Magnesium Iodide.	Zinc Iodide.	Potassium Iodide.	Average.
Magnesium............	2.02		2.00	2.01
Zinc................	1.35	1.23	1.29	1.25
Cadmium.............	1.12	1.12	1.13	1.12.
Aluminium............	.92	.83	.87	.88
Iron.	.69	.6	.74	.68
Cobalt.................	.6	.42	.5	.51
Nickel................		.35	.37	.36.
Tin....................		.72	.69	.71
Lead..................		.82	.85	.83
Copper...............	.63	.67	.62	.64
Silver.	.65	.67	.64	.65
Antimony.....	.41	.47	.46	.44
Bismuth..............	.39	.46	.42	.43

There has been no warping or coaxing of the figures to secure uniformity. The results are given just as they came. If figures were picked out from the different observations it would be possible to obtain almost perfect agreement between the calculations and the determinations, as one may see by looking over the tables.

In regard to the experimental results as given in Tables A, B, and C, it may be stated that all the metals and salts used were

TABLE D.

Comparison of the E. M. F. calculated from the heat of combination and the E. M. F. determined by experiment.

Metals.	Combination with Chlorine Calculated.	Determined.	Bromine. Calculated.	De-termined.	Iodine Calcu-lated.	De-mined.
Magnesium...	3.24	3.1				
Zinc...	2.09	2.11	1.68	1.79	1.05	1 25
Cadmium	2.	1.9	1.58	1.58	.97	1.12
Aluminium...	2.3	2	1.7	1.53	1.00	.88
Iron.	1.75	1.6	1.5	1.3	.85	.68
Cobalt	1.64	1.43				
Nickel........	1.57	1.33				
Tin..........	1.71	1.61	1.5	1.3		
Lead........	1.76	1.63	1.38	1.33	.85	.83
Copper.......	1.4	1.32	1.07	1.02	.69	.64
Silver........	1.25	1.11	.97	.95	.59	.65
Antimony....	1.3	1.22				
Bismuth......	1.3	1.21				

TABLE E.

E. M. F. produced by different metals substituted for the zinc in a Daniell's cell.

Metals.	Volts.	Metals.	Volts.
Zinc.....................	1.08	Lead.......	.58
Cadmium...............	.79	Copper..................	.07
Aluminium.............	.65	Silver...................	.02
Iron.....................	.64	Antimony........	.09
Cobalt..................	.40	Bismuth.....	.17
Nickel....	.1		

chemically pure, with the exception of the metals magnesium and aluminium, and these were of a very good quality. Pure carbon plates were used for the negative plate, but platinum was also tried and gave substantially the same results. The E. M. F. was measured by a Thomson reflecting galvanometer (by Elliott) using two independent standard Daniell cells. One fact which strikes one in looking over the Tables A, B, and C is that the E. M. F. is not very greatly affected by the solution ; a certain metal gives about the same result in one chloride as in another, and the same is true of the bromides and iodides.

In Table E will be found the E. M. F. obtained by substituting different metals for the zinc in a Daniell's cell, but these results being from only one series of observations are probably not so reliable as those in the preceding tables.

In the remaining table are collected in condensed form the principal facts in regard to batteries in which zinc is used as the electro-positive material with the most important electro-negative or depolarizing materials. The facts in regard to metallic zinc, which hold good in all cases in which it is used (no matter what the other material is), are given on a horizontal line with zinc. Below this the facts in regard to each particular combination are given opposite the depolarizer. For example, the data of a zinc and chlorine battery are given on a horizontal line with chlorine, of a zinc and nitric acid (Bunsen) battery on a line with nitric acid.

For convenience the table is divided into two parts; the left-hand side contains the purely scientific data, and the right-hand portion contains the practical facts.

In the first column of the first part are given the chemical symbols reduced to a common basis, any one of the expressions being chemically equivalent to any other. For example, one-half atom of zinc ($\frac{1}{2}$Zn) requires one atom of chlorine (Cl), or one-half atom of oxygen ($\frac{1}{2}$O), or one-third molecule of chromic acid ($\frac{1}{3}$Cr$_2$O$_3$), or one-sixth of the mixture of one molecule of potassium bichromate and seven molecules of sulphuric acid ($\frac{1}{6}$[K$_2$Cr$_2$O$_7$ + 7H$_2$SO$_4$]), and so on.

In the second column are given the chemical equivalents which are simply the proportions by weight required of the different materials. That is, when we use 32.5 grams (hydrogen being assumed as one gram), we require 35.5 grams of chlorine, or 33.4 grams of chromic acid, and so on.

The third column contains the electro-chemical equivalents, which are really exactly the same and directly proportional to the combining weights in the previous column, but are reduced to an electric basis of so many milligrams per coulomb. To convert these figures into grams per ampere hour simply multiply by 3.6.

Symbols. Chemical Expressions reduced to a Common Basis.	Chemical Equivalents. Proportions in which Materials Combine. $H = 1$.	Electro-chemical Equivalents. Weight of Material Consumed per Amp. Sec. Milligrams per Coulomb.	Name of Materials.	Electromotive Force Produced. Volts.	Weight of Zinc Consumed per Horse-power Hour. Pounds.	Weight of Depolarizer Consumed per Horse-power Hour. Pounds.	Weight of Materials Consumed per Amp. Hour in each Cell. Pounds.	Cost of Materials Wholesale. Per Pound.	Total Cost of both Positive and Negative Materials per Horse-power Hour.
$\frac{1}{2}Zn$	32.5	.337	Metallic zinc				.0027	$ .07	
$+$			Used with following electro-negative or depolarizing elements:						
I	127	1.314	Free iodine	1.2	1.67	6.53	.0105	3.50	$22.97
Br	80	.828	Free bromine	1.79	1.12	2.76	.0066	.38	1.12
Cl	35.5	.367	Free chlorine	2.11	.95	1.04	.0029	.02	.17
$\frac{1}{2}O$	8	.083	Free oxygen*	1.9	1.05	.26	.00066		
$\frac{1}{2}S$	16	.166	Free sulphur*	.95	2.1	1.03	.0013		
			CHEMICAL COMPOUNDS.						
$\frac{1}{2}H_2O$	9	.093	Water*	.5	4	1.1	.00074		
HNO_3	63	.652	Nitric acid	1.9	1.05	2.04	.0052	.06	.20
$\frac{1}{3}CrO_3$	33.4	.346	Chromic acid	2	1	1.03	.0027	.20	.28
$\frac{1}{2}CuSO_4$	79.7	.826	Copper sulphate (anhyd.)	1.079	1.86	4.55	.0065	.06	.56
$\frac{1}{2}CuSO_4.5H_2O$	124.7	1.29	Copper sulphate (crystals.)	1.079	1.86	7.13	.0102	.10	.74
$\frac{1}{3}Fe_2Cl_6$	162.5	1.683	Iron perchloride	1.55	1.3	6.5	.0133		
$AgCl$	143.5	1.487	Silver chloride	1.06	1.89	8.32	.0118	16.00	133.25
$\frac{1}{2}Hg_2SO_4$	248	2.57	Mercury sulphate	1.42	1.41	10.7	.0204	.50	5.45
			MIXTURES.					Mixture per lb.	
$\frac{1}{3}\left\{\begin{array}{l}K_2Cr_2O_7 \\ 7H_2SO_4\end{array}\right.$	163.5	1.694	Potass. bichrom, 3 parts $\}$ Sulphuric acid, 7 parts $\}$	2	1	5.03	.0133	.04	.27
$\frac{1}{2}\left\{\begin{array}{l}K_2Cr_2O_7 \\ 4H_2SO_4\end{array}\right.$	229	2.37	Potass. bichrom. 3 parts $\}$ Sulphuric acid, 4 parts $\}$	2	1	7.04	.0186	.05	.42

* Calculated.

In the first column of the second part of the table is given the E. M. F. of each of the combinations. These E. M. F.'s, with the exception of those of oxygen, sulphur, and water, are determined by experiment, most of them being well known and accepted values. In the case of oxygen, sulphur, and water the E. M. F.'s are calculated as explained above and are merely given for comparison. No actual battery corresponding to these materials exists.

In the second column on the right-hand side is given the number of pounds of zinc required per horse-power hour in the case of each combination. For example, a zinc and copper sulphate ·(Daniell) battery requires 1.86 pounds of zinc per horse-power hour of electrical energy produced.

In the next column is given the weight of depolarizer required per horse-power hour in the case of each combination. For example, a battery requires 5.05 pounds of the mixture of three parts of potassium bichromate and seven parts of sulphuric acid, which is about the ordinary strong bichromate solution for porous-cell batteries. Of course the water required for the solution is not considered here or in any of the other figures of the tables, because it costs nothing and serves merely as a medium of electrical action ; but if the total weight of solution is desired, the weight of water must be added.

The weight of the different materials consumed per ampere hour is given in the next column. These figures are obtained directly from the electro-chemical equivalents in the third column by dividing by 125 ; in fact, they are simply the electro-chemical equivalents in pounds per ampere hour.

It should always be carefully noted that the weight consumed per ampere hour is that required in *each cell* in *series,* whereas in the case of horse-power hours the weight given in the table is the total weight used, no matter how many cells there are or how they are arranged.

In the next to the last column is put the wholesale cost per pound of the different materials. These prices are of course very difficult to fix, because they depend upon the market and vary greatly upon the quantities bought ; but the

prices given here are very low, and ordinary consumers would have to pay twice as much in most cases; they furnish, however, some idea of costs.

In the last column is given the cost of both materials, zinc and depolarizer, added together. The values of the products have not been considered, because it is very difficult to estimate the cost of collecting and utilizing residues. In the case of silver chloride the silver resulting from the action would, of course, be worth a large portion of the cost of the original chloride.

One of the interesting points which this table shows is the total weight required per horse-power hour. For example, .95 pound of zinc and 1.04 pounds of chlorine, making a total of almost exactly two pounds, would produce one horse-power of current for one hour if all of the chemical energy could be converted into electric energy.

This brings up the question of how large a percentage of the chemical energy can be utilized, or, in other words, the efficiency of chemical generators. This efficiency is higher, says Professor Crocker, than it is generally supposed to be. No exact figures upon this point are given, but the weight of zinc consumed compared with the theoretical amount having been frequently tested, it is found that even in a plunge battery, where the bichromate solution was directly in contact with the zinc and the opportunity for local action was a maximum, the zinc efficiency was as high as 75 per cent, and in one case 80 per cent. In a porous-cell battery with amalgamated zinc, where there was little or no cause for local action, it is believed that the zinc efficiency would be as high as 90 per cent, and possibly as high as 96 or 97 per cent.

The efficiency of the depolarizer is generally lower than that of the zinc, because there is generally a good deal of chemical energy left in the solution after it is too weak for satisfactory work. The efficiency of the bichromate solution in the plunge battery just referred to was only about 45 per cent of the total theoretical power. But this is very low, because the solution has to be weak in acid on account of

being used in contact with the zinc. In the case of a copper sulphate battery, where the crystals of sulphate are often almost entirely used up, the efficiency might be as high as 80 or 90 per cent.

The efficiency here spoken of is simply the *chemical* efficiency in the battery ; the fall of potential in the battery due to its internal resistance compared to the external is another loss which has to be added to the chemical loss in determining the total efficiency. The possibilities of chemical generators are therefore almost infinite, since it requires theoretically a total of only 2 pounds of zinc and chlorine and 2 pounds of zinc and chromic acid per horse-power hour ; and since the efficiency of batteries can easily be made as high as 75 per cent, it follows that less than 3 pounds of material is actually required per horse-power hour; but unfortunately the water for the solution, the containing vessel, electrodes, etc., are so heavy that the total weight is very many times greater. The possible and the actual battery are thus very far apart. If we use metals of higher chemical affinity and E. M. F. than zinc, the theoretical weight of material required is even less: only one pound total of chlorine and magnesium are required per horse-power hour ; with metallic sodium and free chlorine having a calculated E. M. F. of 4 volts it would only take about .8 pound per horse-power.

The easiest and best solution of the problem, however, does not seem to be the use of more powerful metals than zinc. The latter is powerful enough ; it only takes, as we have seen, about one pound of it per horse-power hour with nitric acid, chromic acid, or bichromate solution, and less than two pounds with copper sulphate. The opportunity for improvement seems to lie more in the direction of perfecting the general form of batteries. The *apparatus* is at fault, not the *chemical action.* Morcover, zinc is about as high on the electro-positive scale as it is safe to go so long as water is present. Even in the case of zinc its affinity for oxygen is greater than that of hydrogen ; it is therefore only by tolerance so to speak, that zinc remains passive in the presence of water. If it is not

properly amalgamated, or if the solution is too strong, local action does occur. If, in place of zinc, we use any more electro-positive metal, these troubles are aggravated ; with magnesium, for.example, there are only very few solutions in which it will stand without great local action.

The proper way to use metals of great chemical energy would seem to be with liquids which do not contain any oxygen, but unfortunately such solutions are not generally good conductors. Another possible plan is to employ a fused electrolyte, but this involves the serious difficulty of maintaining it in the fused state.

So far as is apparent, zinc is a very satisfactory positive material for batteries. After all it is cheaper than any other metal except iron. It is a sufficiently good conductor and less dirty and liable to corrosion than almost any other metal ; it is also, as has just been shown, about as high on the electro-positive list as it is safe to go.

The electro-negative materials, on the other hand, leave far more to be desired. They are generally expensive, very troublesome to handle, and introduce that quality of simple dirtiness to which no other name can be applied, and which is really the most serious objection to batteries. The electro-negatives will, however, do the work, and, as we have seen, it actually requires very little weight to give a great deal of power, if the materials could only be used in a more perfect manner than at present. That seems to be the thing to hope for. Another serious difficulty with batteries is their high internal resistance. A dynamo can easily be made to give 100 volts with a thousandth or a few ten-thousandths of an ohm internal resistance, hence their great output ; but a battery capable of giving 100 volts with only one thousandth of an ohm internal resistance would be of great magnitude.

In this connection it will be interesting to consider how many cells of ordinary gravity battery are required to give one horse-power of current. Each cell will give one volt and not more than half an ampere under normal conditions, hence each cell furnishes half a watt or about 1500 cells to the horse-

power. These cells would, however, give that power for a long time. But the fact remains that that very large number is required to produce the power which a dynamo not much larger than one's hat will generate.

THE RUNNING DOWN OF BATTERIES AS INFLUENCED BY THEIR PERFORMANCE OF MECHANICAL WORK. (LODGE.)

The consumption of material in a battery is simply proportional to the strength of current flowing through it, provided, of course, all local action is avoided. It depends on the quantity of electricity transmitted and on nothing else. The amount of zinc dissolved in every cell of a series battery per ampere hour is accurately known and is 1.21 grams.

Hence any cause which increases the strength of current hastens the running down of the battery, and any cause which opposes the current retards the consumption of material. Now the performance of mechanical work of whatever sort, by a current, necessarily sets up an opposition E. M. F. and weakens the current, as may be proved, and was proved by Helmholtz in 1847, as follows:

Let E be the electromotive force of a battery, supposed constant, and let C be the current flowing round a circuit of total resistance R, resistance also being supposed constant. Then, by definition of E. M. F., the "horse-power," or work done per minute by the current, is EC.

As the current flows round the circuit heat is generated, and this heat was found by Joule experimentally to equal RC^2 per unit of time.

Now if we first suppose that there is no working machine in the circuit—i.e., no machine actually at work: stationary machines there may be as much as one pleases, and they may be holding up weights; but they must not be moving either in the way of raising or lowering them, neither must there be any chemical decomposition going on, or any form of activity other than that already considered in the battery;—given all

these conditions, it follows, by the conservation of energy or the first law of thermodynamics, that

$$EC = RC', \quad \dots \dots \dots \quad (1)$$

an equation which asserts, when we compare it with the Ohm's law definition of $R\left(R = \dfrac{\text{E. M. F.}}{\text{current}}\right)$, that throughout the circuit, under the supposed circumstances, there is no E. M. F., but E.

But now make another supposition: Suppose a working machine, or a decomposition cell, or some other form of activity, introduced into the circuit, whereby the current shall be made to do work—raising weights, for instance, or turning machinery—and let the horse-power of this machine be called P. Then no longer can we equate the power of the battery with the heat produced; we are compelled to take into account every form of energy which is being developed, mechanical or chemical as well as thermal, and so our equation becomes

$$EC = RC' + P. \quad \dots \dots \dots \quad (2)$$

And if again we compare *this* with the Ohm's law definition of $R\left(R = \dfrac{\text{E. M. F.}}{C}\right)$, we find that E is no longer the sole or effective E. M. F. in the circuit, but that the total E. M. F. is $E - \dfrac{P}{C}$. that is, there is an opposition E. M. F., of strength $\dfrac{C}{P}$, and it is natural to consider this opposition E. M. F. as set up in and by the moving machine; or in and by the decomposition cell, if such it be that has been included in the circuit, in which latter case the opposition E. M. F. is known as polarization. And be it noted that it matters not whether decomposition goes on in a special cell or in one of the battery cells—*wherever* it goes on it subtracts its full quota of E. M. F. from the current, and is equally well called polarization.

It is plain, then, that, since by an active machine the total E. M. F. of the circuit is diminished while its resistance remains unaltered, it follows that the current must be weakened. And inasmuch as the wear of the battery depends simply on the current, the wear of the battery is likewise reduced by the activity of the machine.

It is easy enough to write an expression for the strength of the current in terms of the power which the machine is exerting, i.e., the work it is doing per second, by simply solving equation (2); and it is

$$C = \frac{E}{2R} \left\{ 1 + \sqrt{\left(1 - \frac{4RP}{E^2} \right)} \right\},$$

which shows that the greatest possible mechanical power obtainable by perfect appliances from the given circuit is $\frac{E^2}{4R}$: and that when this is obtained an equal amount is expended in generating waste heat. Moreover, it shows that the consumption of material in the battery under these circumstances is exactly half what it is when the machine is held stationary and not allowed to work, and that no slower battery wear than this half-rate is possible, so long as the machine is really worked by the battery and is not driven by some outside power; but that any faster wear is easy, up to the maximum, when the machine is stationary, of $\frac{E}{R}$.

The maximum rate of wear is $\frac{E}{R}$, corresponding to external power o and internal or waste power $\frac{E^2}{R}$.

The minimum rate of wear is $\frac{E}{2R}$, corresponding to external power $\frac{E^2}{4R}$ and internal or waste power $\frac{E^2}{4R}$.

But if the mechanical power obtained be small and insignificant compared with that put forth by the battery, as is

always the case with small-size models which can never be efficient and economical motors, then the rate of wear is so nearly equal to its maximum value $\frac{E}{R}$ as to be indistinguishable from it except by careful measurements.

No more work is called for from the battery, whether a solenoid be sustaining a weight or keeping a piece of iron magnetized, or whether it is doing no such thing. Under all stationary circumstances the whole of the energy is frittered away as heat in the coil; the mere holding up of the weight or keeping a magnet excited involves no direct expenditure of energy.

NOTE.—*Heat Units Corresponding to* 1 *Volt.*—In Professor Crocker's discussion the chemical equivalents used are the half-atomic weights of bivalent substances corresponding to one of hydrogen which is univalent. Hence the volt is taken as corresponding to 23.3 calories. On the other hand, M. Tommasi, in his explanation of the method of chemic constants, evidently uses chemical equivalents which are the atomic weights of bivalent elements and double those of the univalent ones; so that he takes the volt as numerically equal to about twice (46.3) the above valuation.

CHAPTER IV.

SINGLE ELECTROLYTE CELLS.

THE subject is considered under the following divisions:—
    I. Cells having a non-depolarizing electrolyte;
    II. Cells having a depolarizing electrolyte;
    III. Various cells;
    IV. Practical data and tables.

The cells of group I are subdivided into (1) cells having acid solutions; (2) cells having alkaline solutions; and (3) cells having saline solutions.

The cells of group II are subdivided into (1) cells having various solutions; (2) cells having depolarizing negative electrodes; and (3) bichromate cells.

I. CELLS HAVING A NON-DEPOLARIZING ELECTROLYTE.

(I) CELLS HAVING ACID SOLUTIONS.

(a) Cells of the Volta Type.

In the following types depolarization is affected by means of the oxygen of the air.

Volta Cell (1800).—Zinc-copper, weak sulphuric acid. The so-called *couronne de tasses* arrangement is composed of plates of zinc and copper soldered together and bent in horseshoe form. Each couple is plunged simultaneously into two vessels containing weak sulphuric acid. The column form, or "voltaic pile," as it is commonly known, consists of disks of copper and zinc placed alternately one over the other, with intervening

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disks of cloth dipped in diluted sulphuric acid. Frequently the zinc and copper disks are soldered together to form couples separated by the moistened diaphragms. The E. M. F. of the pile (with non-amalgamated zinc) is, according to E. Becquerel, 0.874 volt; to Poggendorff, 0.889 volt; to Reynier, maximum 0.94 volt, minimum 0.194 volt; to Tommasi (theoretic value by method of thermic constants), 0.739 volt. The chemical reaction is the formation of zinc sulphate and disengagement of hydrogen.

Cruikshank's Battery (1801).—A wooden vat coated with marine glue forms the containing vessel. It is divided into numerous compartments by means of metallic partitions formed of plates of copper and zinc superposed and soldered together. All the copper faces are turned in one direction and the zinc faces in the other. The exciting liquid is dilute sulphuric acid.

Wollaston's Battery (1816) (Figs. 30 and 31).—A plate of copper is doubled or folded around a plate of zinc, and insulated therefrom. The containing vessel is glass, the liquid is dilute
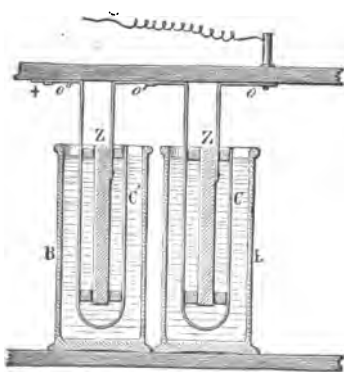

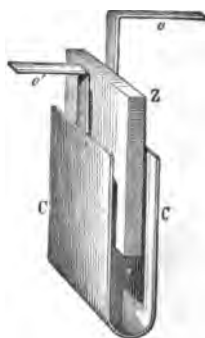FIG. 30.—WOLLASTON'S BATTERY.   FIG. 31.

sulphuric acid, and each pair of elements is supported on a wooden bar, by raising which the plates can be removed from the liquid when the battery is out of use. Modifications of this construction have been devised by Berzelius, Oerstedt, Schmidt, Faraday, and others.

Offershaus' Helical Cell (1821), Fig. 32.—This consists of a containing vessel filled with dilute sulphuric acid in which is placed a plate of zinc and a plate of copper, separated by a net-work of rattan and rolled in helical form. At the moment of immersion this couple gives an intense current capable of reddening fine metal wires, but this soon ceases owing to polarization. The term "calorimotor" was applied to this cell by its designer.

Hare's Battery or "Galvanic Defla-grator" (1824).—Same disposition as the preceding: only the different couples (helices) were fixed on a cross-bar of wood so that all could be immersed at once in the dilute sulphuric acid.

FIG. 32.—HELICAL CELL.

Münch's Battery (1841).—The zinc-copper couples of this battery are disposed in the same way as those of Wollaston, but instead of entering separate vessels they are immersed in a common trough.

Electromotive Force of Trough Batteries.—The E. M. F. of a battery of many zinc-copper, dilute sulphuric acid couples, each of which enters a separate vessel (Wollaston type), is equal to the sum of the E. M. F.'s of the couples. But is it the same when the couples are placed all in one vessel or trough?

Three cases may be considered:

1. If the copper plates have the same surface as the zinc plates, and if the trough is sufficiently large, the E. M. F. of this battery, whatever may be the number of elements composing it, will remain invariable, and equal to that produced by a single zinc-copper couple.

2. If, on the other hand, the plates of copper are bent so as to form metallic diaphragms between each couple as in the Münch battery, and if in the latter the walls of the trough are very close to the metal plates, the E. M. F. will *almost equal* the sum of the E. M. F.'s of the couples. Almost equal,

because a part of the current will always circulate in shunt in the interior of the trough.

3. Finally, if the couples are disposed as in the Cruikshank form, the E. M. F. will be exactly equal to the sum of the E. M. F.'s of each couple.

Modifications of the Volta Cell and its Derivatives. —In order to prevent as much as possible the deposit of hydrogen on the copper plate, Poggendorff (1840), Page (1852), and Walker (1859), following different processes, have covered the previously cleaned surface with electrolyte copper.

Bagration Sand Battery (1844).—Zinc-copper and earth or sand soaked with weak sulphuric acid. Several modifications of this have been made by Cooke, and Brett and Little (1847), the last using a stream of dilute sulphuric acid percolating drop by drop through the sand.

Weare Cell.—Zinc-copper immersed in straw or paper pulp made with dilute sulphuric acid. The zinc and copper are covered with plaster.

Roudel Cell (1860).—Zinc-copper. The copper, which is at the bottom of the vessel, is covered with a mud of potter's clay. Above this the zinc is placed and the jar is filled with a 20 per cent solution of hydrochloric acid.

Pulvermacher's Galvanic Chains (1857).—A battery in the form of a flexible belt, supposed by some people to be useful for curative purposes. Each element of the chain is formed by a zinc and a copper wire wound spirally without touching one another on a small wooden cylinder. Before using, the battery is placed in water acidulated with vinegar. Once impregnated with liquid, it retains its properties for a long time. Very slight moistening suffices. Pulvermacher has also devised a battery consisting simply of a sheet of paper or fabric on which parallel bands of powdered zinc and copper are placed, disposed so that the couples are in tension. The same liquid is employed as in the preceding case.

Smee Cell (1840).—Zinc^{Hg}-platinized platinum or silver and weak sulphuric acid. E. M. F. $= 0.47$ volt. The construction is shown in Fig. 33. Paterson has replaced the

platinized silver with platinized iron. Grove substitutes a gauze of platinized silver wire for the silver plate. Phillips de St. Anstell proposes a platinized tulle (lace), and Walker platinized metallic cloth.

Tyer Cell.—Pieces of zinc in mercury, weak sulphuric acid, platinized silver plate. E. M. F. = 0.5 volt. Poggendorff and Diret have substituted for the platinized plate a copper plate covered with electrolytic copper. Niaudet has replaced the copper plate with one of lead upon which a layer of spongy lead from 1 to 2 mm. in thickness is formed. Ebner has employed a plate of platinized lead.

FIG. 33.—SMEE CELL.

Hughes Cell (1880).—Zinc, hydrogenated iron, acidulated water. E. M. F. = 0.56 volt. The polarization of this couple is about five times less than that of the Smee cell.

According to Grove the E. M. F. of cells of the Smee type remains independent of temperature variations.

Sturgeon Cell (1840).—Zinc^{Hg}-iron, dilute sulphuric acid. The E. M. F. is about half that of the zinc-copper element before its polarization. But when both couples are polarized the E. M. F. of the zinc^{Hg}-iron element is the greatest.

Munnich Cell (1849).—Zinc^{Hg}-Iron^{Hg}, dilute sulphuric acid.

Callan Cell (1855).—Vessel of cast-iron filled with weak sulphuric or hydrochloric acid, to which are added a few crystals of sodium sulphate-Zinc^{Hg}. The object of the sodium sulphate is to preserve the amalgamated zinc and keep its surface clean.

Hulot Cell (1855).—Zinc^{Hg}-aluminium, weak sulphuric acid. The aluminium electrode is placed for a few moments in concentrated hydrochloric acid, which renders it rough and less readily polarized.

(b) Cells with Carbon Negative Electrodes.

Gautherot was the first to observe that in Volta's cell the copper or silver might be advantageously replaced by wood carbon. Later (1825) Cheuvreusse proposed anew to substitute for copper a plate of carbon strongly calcined, or coke from blast-furnaces.

Leuchtenberg Cell (1845).—Zinc^{Hg}-carbon, dilute sulphuric acid.

Fabre de Lagrange Cell (1852).—Zinc^{Hg}-carbon, weak sulphuric acid. The solid carbon electrode is surrounded with fragments of carbon and the whole is contained in a cloth bag. Acidulated water trickles in drop by drop and escapes through a tube from the lower part of the bag and into the outer vessel.

Tommasi Cell (1881).—Zinc^{Hg}-graphite, weak sulphuric acid. The graphite is heated to redness and then cooled in a current of carbonic acid or nitrogen. At the outset the E. M. F. is equal to 1.37 volts, but after a few minutes of closed circuit it falls to 1 volt, and at the end of a few hours to 0.83 volt.

Walker Cell (1859).—Zinc^{Hg}-platinized carbon, weak sulphuric acid.

In the following cells the acidulated solution is maintained by sulphuric acid in a porous cup.

Laborde Cell (Laborde, according to Du Moncel, was the originator of the cell containing concentrated sulphuric acid and water).—Zinc^{Hg}, pure water; in the porous cup, sulphuric acid with five times its weight of water, carbon. Delaurier substituted for the carbon a plate of copper or platinum. According to Du Moncel the addition of potassium nitrate to Laborde's cell augments the E. M. F. and diminishes the resistance. Other inventors, notably Grove, Ferret, and Marseille, have made modifications in the construction of this cell.

R. Napoli Cell.—Zinc, pure water, in a porous cup; a little mercury, concentrated sulphuric acid, carbon. In the Laborde

cell the zinc is placed in the outer vessel, while in this one it is in the porous cup.

Crova and Delhaumuceau Cell.—Zinc^{Hg}, acidulated water; porous cup of carbon filled with sulphuric acid, kept supplied from a glass globe (arrangement of the Parelle and Venté cells). The terminals are lead plates.

According to Laborde it is not advantageous to use concentrated sulphuric acid, as it is not so good a conductor as the dilute or weak acid, and besides produces sulphydric acid and incrustations of zinc sulphate in the pores of the porous cup.

The E. M. F. of these couples with porous cups is equal to the E. M. F. of the zinc-carbon or zinc-copper couple augmented by the E. M. F. developed by the action of the acid in the porous cup upon the water in the external vessels.

(c) Cells having Mechanical Movements.

E. Becquerel Cell (1852).—This is a Smee cell in which the platinum plates of each couple are moved mechanically alternately into acidulated water and into the air. E. M. F. $= 0.79$ volt. With a carbon negative $E = 1.04$ volts.

Erckmann Cell.—The couples are formed of disks of zinc^{Hg} and of copper mounted on a common axis which is rotated by mechanical means. These disks are about half immersed in insulated troughs containing dilute sulphuric acid. Brushes are fixed on the frame of the apparatus between the metallic surfaces of the disks. As the axis revolves each half-disk passes alternately into the acidulated water and the air, and meanwhile is rubbed against the brushes. According to Erckmann there are no variations in the strength of the current yielded, the maximum energy being maintained.

L. Malche Cell (1864).—Iron-copper or iron-carbon and water, with 1 per cent of nitric acid. The iron is in the form of a hollow cylinder like the zinc in many well-known cells. The copper or carbon electrode is a vertical disk supported on a shaft, which disk enters for about one third its area in the exciting liquid. When the cell is in operation the shaft is rotated.

All parts of the disk therefore pass alternately through the exciting liquid and through the air, so that the accumulated hydrogen is thus enabled to escape. Polarization is said to be almost entirely prevented, and according to Maîche the E. M. F. is a little higher than that of the Daniell cell.

Skene and Kuhmaier Cell.—Zinc-copper and dilute sulphuric acid. The copper is mechanically moved alternately into the liquid and into the air. A simple clockwork mechanism suffices to operate a large number of elements which maintain the same intensity for quite a long time.

Pulvermacher Cell. — Zinc^{Hg}-platinum, dilute sulphuric acid. E. M. F. = 1.16 volts. Dilute sulphuric acid is placed in a porous cup containing a zinc rod. The platinum is disposed in the form of a spiral spring around the cup. The air acts as a depolarizer. On replacing the dilute acid with a potash solution, and the platinum with silver, the E. M. F. becomes 1.5 volts.

Chardin Cell (1886).—Zinc^{Hg}-carbon and an exciting liquid composed of hydrochloric acid 1 part, alcohol 2 parts, and water 3 parts. E. M. F. = 1.2 volts.

Influence of the Negative Electrode on the E. M. F. of Cells of the Type Zn–R.H$_2$So$_4$Aq.—The experiments of Exner (1880) show the following facts :

1. That in single-liquid cells in closed circuit the nature of the negative electrode R has no effect on the E. M. F.

2. That the E. M. F. on closed circuit does not depend on the intensity of the current.

3. That if the E. M. F. found by experiment is greater than that indicated by the chemical data, this is due to oxygen dissolved in the water.

4. That if the E. M. F. is less than the theoretical value, this is due to the sulphate of zinc produced in the cell which, by diffusion, is carried to the negative electrode R.

D. Tommasi (1880) finds that two zinc-platinum dilute sulphuric acid couples do not decompose a potassium sulphate solution. In fact, the sum of 38 cal. + 38 cal. (calories disengaged by the zinc-platinum couple) is less than 103 cal., or the

calories absorbed by the decomposition of dissolved potassium sulphate. By using, however, two zinc-carbon dilute sulphuric acid couples it is easy to decompose a saturated solution of potassium sulphate, with very marked disengagement of gas at the platinum electrodes and transportation of the acid to the negative electrode from the base at the positive electrode. If the E. M. F. of the zinc-carbon couple be compared with that of a zinc-copper or zinc-platinum couple, the following results appear :

	E. M. F.'s	
Couples.	Maxima.	Minima.
Zinc-platinum (platinized).	1.56 volts.	0.71 volt.
Zinc-carbon	1.38 "	0.44 to 0.30 **volt.**
Zinc-copper	0 96 "	0.53 volt.
Zinc-platinum ....,...	1.41 "	0.6 "

In these couples the zinc was amalgamated and the exciting liquid was composed of 100 c. cm. of water and 5 c. cm. of sulphuric acid (A. Naccari and G. Guglielmo, 1881).

On the other hand, Berthelot has obtained the following values :

	E. M. F.'s	
Couples.	Maxima.	Minima.
Zinc-platinum..		0.47 volt.
Zinc carbon..	1.37 volts.	0.83 "

Influence of the Negative Electrode on the Quantity of Calories Transmissible to the Circuit in the Form of Chemical Energy.—D. Tommasi (1880) has determined the singular fact that the E. M. F. of the same couple varies according as the negative electrode is platinum or carbon. Such a couple, for example, although incapable of electrolyzing water or a saline solution (despite the fact that the calories disengaged were more than the calories absorbed by the decomposition of the electrolyte) with a platinum electrode, attained this capacity when a carbon electrode was substituted. Thus, a magnesium-platinum dilute sulphuric acid couple ought theoretically to

decompose water. The number of calories disengaged by the action of magnesium on sulphuric acid (112) is obviously greater than the number of calories (69) absorbed on the decomposition of water. Nevertheless electrolysis does not take place ; and the result is the same if copper or silver be substituted for the platinum. But if a cylinder of graphite or retort carbon be used as the negative electrode, then electrolysis occurs. Chromic-acid cells follow the same rule.

(2) CELLS HAVING ALKALINE SOLUTIONS.

Bennett Cell (1883).—External vessel of glass filled with iron turnings moistened with a potash solution; porous cup, solution of potash, zinc.

Fabri and Ravaglia Cell (1884).—Zinc^{Hg}.carbon, solution of caustic potash. The carbon is surrounded with fragments of carbon and contained in a porous cup. E. M. F. = 1.6 volts. After polarization E. M. F. = 0.9 to 1 volt. The product of the chemical reaction is zincate of potassium and hydrogen.

(3) CELLS HAVING SALINE SOLUTIONS.

(a) Ammonium Chloride.

According to F. Salva (1804), Volta first recognized ammonium chloride to be one of the best exciting liquids. He says: " The substances which the different physicists have mixed with water are chloride of sodium, hydrochlorate of ammonia, sulphate of alumina, sulphate of iron, potash, and sulphuric, nitric, and hydrochloric acid more or less weakened. But Volta has positively declared to the National Institute of Paris that, of all these, he prefers to add hydrochlorate of ammonia to water in order to produce violent shocks through the agency of the pile which bears his name."

L. Matche Cell (1879).—This is probably the most ingenious

of all the cells which use atmospheric oxygen as the depolarizer. In the form shown in Fig. 34 the outer vessel of glass has an ebonite cover, to which is attached an annular perforated vessel of porous earthenware. The latter is traversed by an ebonite tube which carries a small porcelain cup. In this cup are placed a small quantity of mercury and pieces of zinc, in the shape of ingots, weighing some 50 grams each. The annular porous vessel is filled with crushed and platinized retort carbon. Platinum black will condense in its pores 745 times its volume of hydrogen; and since it is applied to the carbon in an excessively thin film, the cost of platinizing is small.

FIG. 34.

To one of the pieces of platinized carbon is attached a platinum wire which connects with one of the binding posts of
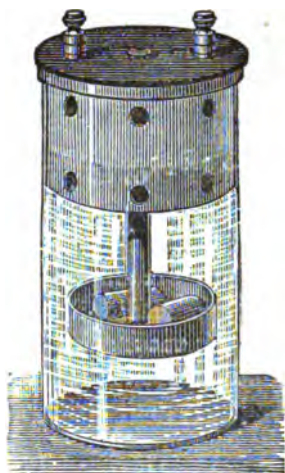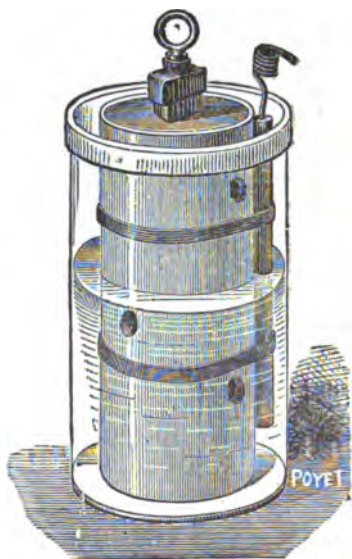

FIG. 35.—MAÎCHE CELL.

FIG. 36.—MAÎCHE CELL.

the cell. To the other binding post is secured a similar platinum wire which is led through the supporting tube to the mercury in the porcelain cup. The liquid contains 15 per cent of ammonium chloride, and its upper level reaches about 2 cm. above the lower edge of the annular vessel containing the carbon. By this means the carbon is kept always moist by capillarity, and the atmospheric oxygen has free access to it. With this oxygen the hydrogen condensed in the pores of the platinum film combines, and thus there is constant depolarization. The consumption of zinc appears to be closely proportional to the intensity of the cell, and on open circuit the oxidation of the zinc does not reach 1 milligram per day. The arrangement of the carbon electrode at a distance from the bottom of the cell is very advantageous, as the zinc salts falling to the bottom are thus prevented from reaching it. Their electrolysis is also avoided, and no zinc becomes precipitated upon the carbon. E. M. F. = 1.25 volts. Various modifications of this cell are shown in Figs. 35, 36, and 37. Those represented in
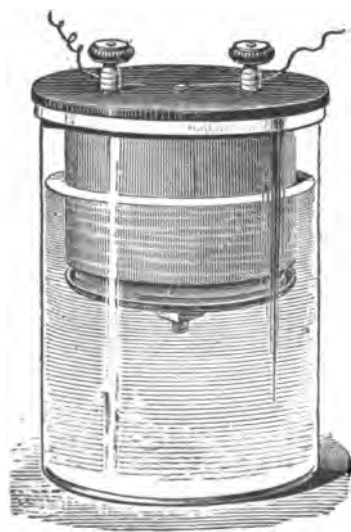

FIG. 37.

Figs. 35 and 36 are employed in the French railway service. In the form known as Fig. 37 a disk of zinc is disposed below the porous cup, and is connected to the binding post by a platinum wire. This model was devised especially for telegraph and telephone service. Other types of Maiche's cell have parallel plate electrodes of the ordinary form, and employ a special neutral saline solution known as "électrogène," the composition of which is not published, but which is stated to produce no crystallizable sub-salts and to be capable of operating the cell four times as long as an equal quantity of water saturated with ammonium chloride.

The Law Cell (1882) (Fig. 38).—Zinc-carbon solution of ammonium chloride. $E = 1.5$ volts. The principal feature here is the abnormally large surface of the carbon electrode, which, as shown in Fig. 22, is a double cylinder.

Other forms of this cell are represented in Figs. 39 and 40.   In Fig. 39 the corrugated carbons are fastened to a central block of carbon, which is wedge-shaped and fits into a corresponding opening in the lid.   In this manner the carbons are prevented from falling, and as an additional safeguard the central piece is cemented to the lid, so that no movement is possible.

FIG. 38.—LAW CELL.

In the form shown in Fig. 40 the negative electrode consists of a corrugated cylinder bolted to a conducting carbon which passes up through the glass cover

FIG. 39.—LAW CELL.   FIG. 40.—LAW CELL.

and serves as the attachment for the binding post.   In order to avoid the creeping of salts the conducting plate is saturated

with paraffine, and to prevent all action on account of the clamping device, the bolt and the nuts which secure the cylinder to the conducting plate are made of hard rubber. One side of the cylinder, it will be noted, is hollowed out, and in this space the zinc passes down from the cover.

Bagration Cell (1844).—A plate of zinc and a plate of copper embedded in sand moistened with ammonium chloride.

Prax Cell.—A plate of zinc and a plate of copper separated by five layers of flannel and two paper diaphragms soaked in a solution of ammonium chloride and dusted over with ammonium chloride in powder.

Fortin Cell.—Zinc^{Hg}, solution of ammonium chloride; porous cup filled with crushed retort carbon moistened with ammonium chloride and enclosed in a carbon cylinder. E. M. F. = 1.084 volts

Devos Cell.—Glass vessel divided into two compartments by a plate of carbon; in one is a mixture of crushed coke and ammonium chloride, in the other a plate of zinc. The vessel is filled with water.

Lionel-Weber Cell.—Zinc^{Hg}, ammonium chloride solution, porous vase filled with plumbago, carbon.

Chemical Reactions in the Ammonium Chloride Cells. —Zinc dissolves in a solution of ammonium chloride with disengagement of hydrogen and formation of ammonia and a double chloride which remains in solution in the ammonium chloride (on open circuit even non-amalgamated zinc is not perceptibly attacked by this solution). This double chloride forms in isolated crystals on the zinc, having the composition $Zn(N.H_4Cl)_2$. The crystals are partly decomposed by the water and yield an insoluble body represented by $OH-Zn-NH_4Cl$ (Divers).

Davis considers the composition of the crystals deposited to be represented by the formula $ZnH_4O_2.ClNH_4$; and Ferray, by the formula $3Cl_2Zn, 8NH_3, 4H_2O$.

According to Ferray, the decomposition of the crystals in presence of water takes place in the following manner:

$$3Cl_2Zn, 8NH_3, 4H_2O = 6ClNH_4 + 2NH_3 + H_2O + 3ZnO.$$

The hydrogen due to the action of the zinc on the ammonium chloride goes to the carbon, where it is apparently burned * by the atmospheric oxygen stored in the pores of the carbon, the depolarization of the cell thus being assisted. Ferray has analyzed the gases evolved from these couples, and has found—

1. After a prolonged closing of the circuit: hydrogen.

2. At the beginning of the action: $\frac{1}{2}$ volume of hydrogen, $\frac{1}{3}$ volume of nitrogen and carbonic acid, $\frac{1}{6}$ volume of CH_4.

As the result of experiment upon these couples H. Sauvage (1875) concludes:

1. The carbon should be protected from all deposits which might retard absorption of air.

2. The carbon surface should be as large as possible, and the part exposed to the air should be at least equal to that which is immersed in the liquid.

3. The best carbon to use is retort carbon in large fragments.

(b) Chloride of Sodium.

Zaliwski Cell.—Zinc, carbon, solution of sodium chloride.

Cauderay Cell.—A hollow cylinder of carbon containing a plate of non-amalgamated zinc and immersed in a sodium chloride solution.

Palagi Cell (Pile à Chapelet).—A long glass test-tube containing a solution of sodium chloride in which are immersed a zinc plate and a chain of fragments of carbon linked together by pieces of copper wire.

Duchemin Electric Buoy.—A cylinder of carbon and plate of zinc fastened to a buoy and floated in sea-water.

Chemical Reactions of the Sodium Chloride Cell.—The zinc in presence of the sodium chloride decomposes the water with disengagement of hydrogen and formation of zinc oxide, which dissolves in the sodium chloride, forming a double chloride of zinc and sodium which deposits in crystalline form.

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* Not experimentally demonstrated as yet.

(c) Various Salts.

Du Moncel Cell (1856).—The porous cup of this cell contains a paste formed of powdered carbon, wood sawdust, and a solution of ammonium nitrate. In the external vessel, around the porous cup is another paste formed of zinc filings, wood sawdust, and ammonium nitrate. In each vessel a copper wire is inserted as a conductor.

Stohrer Cell.—Zinc^{Hg}, carbon, solution of alum. There is a disengagement of hydrogen and formation of zinc sulphate and a crystalline precipitate having, according to Debray, the composition

$$8Al_2O_3, 5SO_3, 25H_2O.$$

Boettger Cell (1867).—Hollow cylinder of zinc in which a carbon cylinder is inserted. In the annular space between the cylinders is loosely packed a mixture of magnesium sulphate and sodium chloride moistened with a concentrated solution of the same salts.

Buchin and Tricoche Cell (1884), Fig. 41.—Several cylindrical carbons and one zinc cylinder immersed in a potassium bisulphate solution. The bisulphate dissolving in water decomposes into neutral sulphate and sulphuric acid, which reacting on the zinc gives zinc sulphate and hydrogen.

FIG. 41.—BUCHIN AND TRICOCHE CELL.

Selmi Cell (1867).—Zinc-copper solution of potassium sulphate. The zinc cylinder is placed at the bottom of the jar. The copper in the form of a spiral is at the centre of the cell and is immersed for but a few millemeters. E. M. F. = about 1 volt. The chemical reactions are (1) decomposition of the potassium-sulphate into sulphuric acid and potash; (2) formation of zinc sulphate and disengagement of hydrogen; (3) decomposition of the zinc sulphate by the potash. Whence it results that in this cell the only definite product is zinc oxide. The

potassium sulphate becomes regenerated indefinitely, as the potash set free precipitates the zinc oxide from the sulphate as fast as the latter is formed.

Schanschieff Cell.—The electrodes employed are the usual carbon and zinc, but the solution is a mercurial sulphuric acid compound which is prepared as follows: To 3 pounds of sulphuric acid, specific gravity 1.846, there is added 2 pounds of metallic mercury. This is boiled until the metal is converted into mercuric sulphate, and the heat maintained until the excess of acid is evaporated and the salt is dry. When cold, one gallon (ten pounds) of water is added. This dissolves a part only, precipitation of basic sulphate of mercury taking place. The solid residue is separated, and this is then again boiled with sulphuric acid, as before, in the proportion of two parts of the residue to three parts of acid. By boiling, the residue is dissolved, and by continuing the heat the excess of acid is evaporated. The resulting mass, when cold, is added to the original solution, and again there is dissolved as much as the solution will take up, and the residue separated. After three or four repetitions the whole is dissolved in the original gallon of water. The density of the liquid will then be about 1.425 Baumé, and the quantity about 5 quarts. Finally, the liquid is evaporated by heat until the electro-salt is deposited in a solid crystalline state. This is raked out as it falls and packed in closely-stoppered bottles, in which it may be kept for an indefinite time. The salt thus produced consists of a combination of yellow basic sulphate of mercury (known as "turbeth mineral") with bisulphate of mercury, the formula being $2HgO,SO_4 + HgSO_4 + 3H_2O$. The solution of this salt is of higher specific gravity than any mercurial salt heretofore produced. When liquid is required for use in a battery, 5 pounds of the salt are dissolved in 1 gallon of water.

Blair Cell.—Zinc-tin, concentrated solution of potassium carbonate. The zinc and tin are separated by a layer of wood charcoal. The zinc is covered with canvas.

Jourdan Cell (1880).—Zinc-plumbago, solution of silicate of soda. The containing vessel is made of plumbago, and so

serves, at the same time, as the negative electrode.   According to Jourdan, this cell has, when of the same dimensions, the same E. M. F. and the same resistance as the Callaud cell.

La Valette and Delaurier Cell.—Zinc-copper, solution of zinc chloride.   The chemical reaction yields zinc oxychloride and hydrogen.

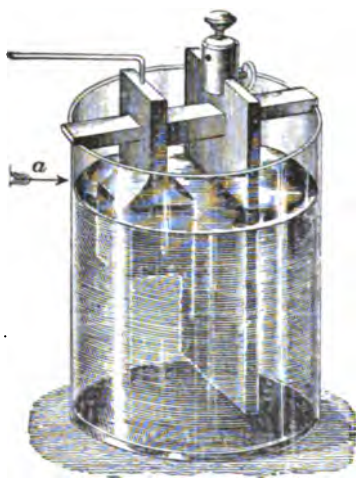*C. Pabst Cell* (1886).—Iron-carbon, solution of zinc chloride. E. M. F. = 1 to 1.2 volt.   This cell, as represented in Fig 42, has, as electrodes, a plate of carbon prepared with zinc oxide and a block of iron, both suspended to a cross-bar which rests on the upper edge of the containing vessel and entering a solution of zinc chloride of definite composition.

FIG. 42.--PABST CELL.

Bréton Portable Cell.—Mixture of zinc, wood, and chloride of calcium in powder ; mixture of copper, wood, and chloride of calcium in powder.   Each compound is contained in a canvas bag enclosed in a box.   Claimed to be useful for medical purposes. In operation the two bags are taken out of their boxes, connected by a wire, and applied to the human body.

Coiffier Cell.—Earthenware exterior vessel containing a zinc cylinder within which is a prism of retort carbon.   In the space between the outer vessel and the zinc, and the zinc and the carbon, is moistened earth.   E. M. F. = 0.76 volt.

Torregiani Cell (1866).—Lead-carbon and solution of potassium or sodium carbonate.   The result of chemical reaction here is carbonate of lead, potash, or soda and hydrogen.

Bartoli and Papasogli Cell.—Carbon-platinum or gold, and saturated solution of sodium carbonate.   E. M. F. = 0.10 to 0.17 volt.   With a solution of hypochlorite of soda, E. M. F. =

·0.4 to 0.5 volt. If graphite be substituted for retort carbon in the hypochlorite, E. M. F. = 0.2 volt.

Mouthiers Cell (1867).—Zinc-carbon, solution of ammonium carbonate. Chemical reaction is as follows: The zinc dissolves with disengagement of hydrogen, forming a granular precipitate which appears to be a mixture of zincate of ammonium and of zinc carbonate.

Jablochkoff Cell (1884).—First Model. This cell is composed of a thin plate of sodium to which is applied a small plate of amalgamated copper which serves as an electrode. The sodium plate is covered with silk paper and placed on a plate of very porous carbon. E. M. F. = about 2.5 volts, which varies with the temperature and with the hygrometric state of the air. Under the influence of the moisture of the air, the sodium oxidizes, becoming transformed into caustic soda, which escapes as fast as produced, thus always exposing a new surface of the sodium.

Jablochkoff Cell (1885).—Second Model. Commonly termed the "auto-accumulator." This consists of a flat trough of carbon covered externally with paraffine, in which are placed pieces of oxidizable metal, which may be sodium or amalgam of sodium, zinc, or iron. The carbon cup is then filled up to its edges with any spongy material, such as wood sawdust, packing cloth, etc. There are two conditions of its use: if sodium be employed, it is not necessary to introduce water, the oxidation of the sodium forming caustic soda attracting sufficient moisture of itself; if, however, the metal employed is zinc or iron, the spongy mass is wet with a solution containing sea-salt—preferably calcium chloride, which attracts and holds the moisture. Finally, upon the spongy mass which is flattened on its upper surface are placed a number of tubes of porous carbon. E. M. F. depends upon the oxidizable metal which is employed. With amalgam of sodium, it is 2.2 volts; with zinc, 1.6 volts; with iron, 1.1 volts.

Reynier Standard Cell.

Surface of copper electrode................$30d^2$
Surface of amalgamated zinc electrode.... $0.3d^2$

Liquid : 800 c. cm. solution of sodium chloride for
  1000 c. cm. of water.
E. M. F...................................... .. 0.82 volt.
Resistance. .... 1–2 ohms.

The E. M. F. of the standard naturally depends on the
liquid contained. It is not the same with amalgamated as
with ordinary zinc. The following values have been found
with different liquids :

Acidulated water (sulphuric)... { ordinary zinc... 0.94 volt.
                                 { amalg. " .... 1.072 "
Solution of sodium chloride.... { ordinary " .... 0.78 "
                                 { amalg. " .... 0.82 "
Solution of zinc chloride...... { ordinary " .... 0.85 "
                                 { amalg. " .... 0.86 "
Solution of zinc sulphate...... { ordinary " .... 1.00 "
                                 { amalg. " .... 1.04 "
Solution of caustic soda....... { ordinary " .... 1.06 "
                                 { amalg. " .... 1.09 "

Ayrton and Perry Standard Cell.—Zinc-copper, saturated
solution of zinc sulphate. In order to avoid polarization, a
condenser is used. E. M. F. = 1 volt. For other standard
cells see the standard cells of Latimer-Clark, Regnault, Warren
de la Rue, Kittler, Lodge, London Post Office, Weston, and
Carhart.

**Action of the Air on Couples having a Single Electro-
lyte not Depolarizing.**—Prior to 1801, Van Marum showed
that the voltaic pile gained in energy when placed in a reser-
voir filled with oxygen. At about the same time, Pepys ob-
served that when the pile operated in air there was an absorp-
tion of gas, and that the presence of oxygen tended to increase,
while that of nitrogen tended to decrease the action of the pile.
Some time afterwards, Biot and Cuvier also observed that there
was a gaseous absorption in a pile formed of disks of zinc and
copper and of cloth soaked in a solution of aluminium sulphate.
It was also then remarked that the action of the pile slackened.

but became renewed after the introduction of a new quantity of air. Adie (1848) found that a small element of zinc and platinum, which in aerated water gave a deviation of 3.5 degrees, produced a deviation of only 0.5 degree in boiling water ; and he furthermore determined that the presence of oxygen was simply useful, but not necessary, to the production of the current.

CHAPTER V.

SINGLE ELECTROLYTE CELLS. (*Continued.*)

II. Cells having a Depolarizing Electrolyte.

(1) cells having various solutions.

Broglio Cell.—Zinc-carbon, concentrated solution of bi-·sulphite of potassium or sodium. Zinc dissolves in these solutions without disengagement of hydrogen, and hence there is no polarization at the carbon electrode. The electromotive force of this cell, according to Broglio, is very nearly equal to that of the bichromate couple, but its lifetime is much longer. The zinc is attacked even on open circuit. The result of chemical reaction is the formation of sulphite of zinc, alkaline sulphite, and of hydrosulphite, SO_3KH or SO_3NaH.

Roberts Cell (1852).—Tin-platinum, dilute nitric acid. The intensity of this cell, according to Moigno, is very great. Fifty small cells of 16 cm. height and 11 cm. diameter are capable of disengaging instantaneously 21 c. cm. of gas. The results of chemical action are the disengagement of nitrous oxide, N_2O, and there is formed metastannic acid, $Sn_5O_{11}(H_2O)_4$, nitrate of ammonium, and nitrate of tin.

Boettger Cell (1867).—Carbon vessel covered externally with a varnish and filled with a solution of ferric sulphate in which is plunged a cylinder of amalgamated zinc. The results of chemical action are reduction of ferric sulphate into ferrous sulphate and formation of sulphate of zinc.

Pabst Cell (1884).—Wrought-iron, carbon, dilute solution of ferric chloride. E. M. F. = 0.78 volt. Chemical reaction: reduction of ferric chloride into ferrous chloride.

Figuier Cell (1863).—Zinc-carbon or iron-carbon, concentrated solution of ferric chloride and sulphate. According to Figuier, a single element will decompose water, from which it appears that the E. M. F. is equal at least to 1.5 volts. When the cell is run down, a current of chlorine is passed through the liquid, which brings the ferrous salts back to ferric salts.

Chemical reaction : the ferric chloride and sulphate are reduced by the hydrogen to the state of ferrous chloride and sulphate. When zinc is employed, zinc chloride and sulphate are also formed.

Fonvielle and Deherain Cell (1858).—Zinc^{Hg}-copper, binoxide of hydrogen to which 10 per cent of hydrochloric acid is added. This cell is said to give a stronger current than the Wollaston cell.

Desbordeaux Cell (1844).—Zinc-copper, solution of zinc sulphate containing a little copper sulphate. The couples are disposed like those of the Wollaston cell. This cell has the grave objection of producing local couples owing to the deposit of copper on the zinc.

Laurie Cell (1881).—Zinc^{Hg}-carbon, solution of iodine in iodide of zinc. E. M. F. = 1 volt. The zinc is attacked even in open circuit.

Defonvielle and Humbert Cell.—Zinc^{Hg}-carbon, water saturated with chlorine to which 10 per cent of hydrochloric acid is added. A current of chlorine is occasionally passed through the liquid. Chemical reaction : the zinc attacks the hydrochloric acid and produces zinc chloride and hydrogen, and the latter, instead of being disengaged, combines with the chlorine and re-forms hydrochloric acid.

Eisenmann Cell (1886).—Zinc^{Hg}-carbon, solution of sodium tungstate. This solution is made by dissolving in 350 c. cm. of water 30 grams of sodium tungstate and 5 grams of sodium phosphate, and adding to the solution a small quantity of sulphuric acid.

Mouthiers Cell (1867).—Zinc-carbon, concentrated solution of ferrous sulphate. Chemical reaction : the zinc is dissolved with disengagement of hydrogen and ferric hydrate is precipi-

tated, resulting from the oxidation of the ferrrous hydrate. It may appear strange at first sight that ferrous hydrate can become oxidized when in the presence of such a reducing agent as hydrogen (H + cal.) ; but it appears from the experiments of D. Tommasi that hydrogen disengaged under these conditions is not apt to reduce ferric hydrate.

Laurie Cell (1886).—Cadmium-platinum, solution of iodide of cadmium to which iodine is added. E. M. F. = 1.076 volts. The cadmium plate is rotated so as to traverse the exciting liquid three or four times a second by means of clockwork mechanism.

Aymonnet Cell (1886).—Iron-carbon, aqua regia diluted with water. E. M. F. = 1.3 to 1.1 volts. The principal chemical reaction is represented by the following equation :

$$2Fe + 6HCl + 2NO_3H = Fe_2Cl_6 + 4H_2O + 2NO.$$
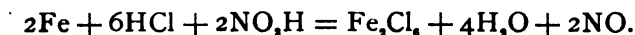
but there is formed, besides, a small quantity of nitrate of iron and of ferric hydrate, which dissolves in ferric chloride.

Fyfe Cell (1837).—Zinc-iron and a solution containing copper sulphate, potassium nitrate, and sodium chloride.

Zaliwski-Mikorski Cell (1869).—Copper-carbon and a mixture of sulphuric and nitric acids diluted with water.

D. Tommasi Cell (1866).—Magnesium-platinum or magnesium-carbon, solution of mercuric sulphate in water saturated with sodium chloride. The mixture is made hot, and on cooling is filtered. E. M. F. = 1.7 volts.

Lobstein Cell.—This consists of a lead vessel on the bottom of which is placed a plate of zinc and a plate of copper. The exciting solution consists of lead acetate 400 grams, sodium chloride 400 grams, sulphuric acid 1000 grams, and water 1000 grams. This cell was devised for "galvanizing" iron.

Wheatstone Cell.—This is a Daniell cell with a single electrolyte. It consists of a pasty amalgam of zinc contained in a porous vessel, solution of copper sulphate and copper. Chemical reaction: decomposition of sulphate of copper, formation of zinc sulphate, and deposit of metallic copper.
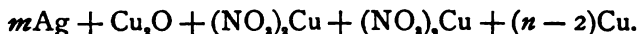
Gladstone and Tribe Cell (1872).—Copper-silver; six per cent solution of copper nitrate. The copper plate is immersed entirely in the solution, while the silver plate, which is in the form of a flattened cup, is in contact with the solution only at its lower part. The two plates are placed horizontally in the liquid. Chemical reaction : the copper nitrate decomposes with formation of cupric oxide which is deposited on the silver, and the copper of the couple enters into solution and regenerates the nitrate.

The following formulæ may serve to render more intelligible the change and the chemical transportation :

Before contact :

$$m\mathrm{Ag} + \mathrm{O} + (\mathrm{NO_3})_2\mathrm{Cu} + (\mathrm{NO_3})_2\mathrm{Cu} + n\mathrm{Cu}.$$

After contact :

$$m\mathrm{Ag} + \mathrm{Cu_2O} + (\mathrm{NO_3})_2\mathrm{Cu} + (\mathrm{NO_3})_2\mathrm{Cu} + (n - 2)\mathrm{Cu}.$$

This action evidently continues until the copper is used up, the oxygen being furnished by the air ; whence the name "air-cell" which has been given to the element. By employing a solution of deoxygenated copper nitrate, an excessively weak current is obtained, which is probably due to the difficulty of completely eliminating air from the solution, and to a certain quantity of oxygen condensed on the surface of the silver.

(2) CELLS WITH NEGATIVE DEPOLARIZING ELECTRODES.

Ritter Cell.—Zinc-tellurium, dilute sulphuric acid. The tellurium absorbs hydrogen, producing hydrotelluric acid, $H_2\mathrm{Te}$.

Woodward Cell (1890) (Fig. 43).—In this, advantage is taken of the depolarizing property of the oxide of copper. The positive electrode is zinc sponge. The negative electrode, *B*, is made by taking a piece of iron of requisite size and shape, placing around it a jacket, *C*, of perforated iron, and filling the space between the casing and the piece of iron with

oxide of copper and iron filings or turnings, *D.* By this construction a large conducting surface is secured, while rapid
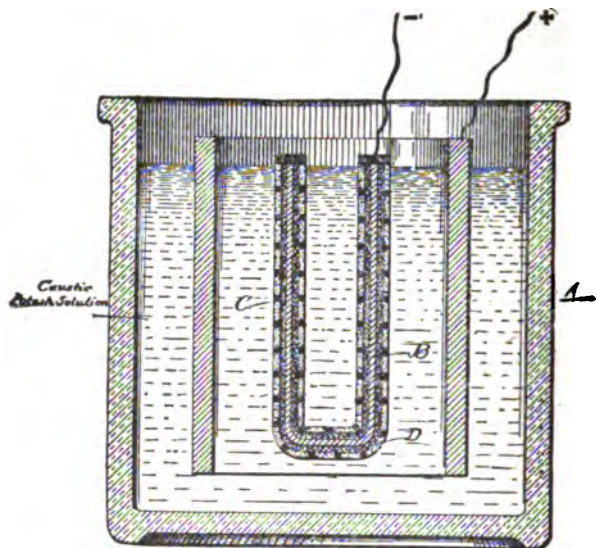

FIG. 43.—WOODWARD CELL.

polarization is prevented. The electrode is placed in a caustic-potash solution in a cell with the zinc sponge.

Dun Cell (Fig. 44).—The negative electrode of this element is formed by a hollow cylinder of coke, fitted with a bottom and partly filled with small coke. The positive electrode is formed of a cylinder of zinc surrounding the former and separated from it by two rings of caoutchouc ; the whole is contained in a glass vessel.

Permanganate of potash is introduced into the cylinder of coke, and the entire element is filled with a lye of caustic potash in the proportion of one part of potash to five of water. The permanganate dissolves in the potash, and acts as an oxidizer and depolarizer on the surface of the coke.

It is claimed that in the state of rest this cell is not impaired, that the zinc consumed is proportional to the quantity of electricity produced, and that there is no escape of gas.

The constants of a Dun cell of the size of an average Bunsen are: electromotive force, 1.8 volts; current on short circuit, 15 to 20 amperes; internal resistance (calculated), 0.09 to 0.12 ohm. After 30 to 40 minutes on short circuit the electromotive force falls to 1 volt, and the current to 8 or 10 amperes, an intensity which it then retains for a long time. The cell is regenerated after one or two hours' rest, and

FIG. 44.—DUN CELL. FIG. 45.—POLLAK CELLS.

recovers the electromotive force indicated. In the case of the production of feeble currents the depolarization is complete and the cell is constant.

The exhausted liquid, which contains the zinc consumed, may then serve for coating metals with zinc, especially iron, without the need of an auxiliary battery. An electrode of zinc and the object to be coated are sufficient.

Pollak Cell.—The cell, which is shown in two forms in Fig. 45, consists of a glass jar upon the bottom of which rests a cylinder of zinc, which constitutes one electrode. The other electrode is a carbon cylinder, which, though very porous, is made to conduct well, and has a coating of copper deposited electrolytically upon its lower end. After the electrodes are placed in position, common salt or sal-ammoniac is put into the

vessel, which is then filled with water up to about 3 or 4 centimetres above the lower end of the carbon.

At the beginning local action takes place between the copper deposited on the carbon and the carbon itself, which decomposes the salt used, so that it forms copper compounds. If sal-ammoniac be employed, copper chloride is formed, by which the liquid near the copper is colored blue. The nascent hydrogen liberated at the surface of the copper decomposes the copper compounds, which are, however, again formed by the action of the carbon; in other words, the cell keeps charging itself continuously. The results of a continuous test of the element closed through 10 ohms external resistance for a period of 670 hours gave the following mean values: E. M. F. = 0.932 volt, current = 0.0846 ampere; internal resistance = 1.016 ohms.

(3) BICHROMATE OF POTASSIUM CELLS.

Poggendorff Cell (1842).—Zinc^{Hg}-carbon, solution of potassium bichromate to which sulphuric acid is added. The bichromate solution consists of water 18 parts, potassium bichromate

3 parts, sulphuric acid 4 parts. Grenet (1856) has given to this cell the shape of a bottle, as shown in Fig. 46. The zinc is here arranged so that it can be drawn out of the liquid when the cell is not in use. Grenet's solution consists of water 1000 grams, potassium bichromate 100 grams, and sulphuric acid 300 grams. In certain forms of the Grenet cell a lead tube is arranged so as to blow in air and thus agitate the liquid—an operation which tends to prevent the deposition of chromium oxide on the zinc, and also to

FIG. 46.—GRENET CELL.

contribute to the depolarization of the carbon.

Aboilard Cell.—The peculiar feature of this cell is that its operation is prevented at will by moving the zincs into a special chamber (see Fig. 47). The exciting liquid consists of
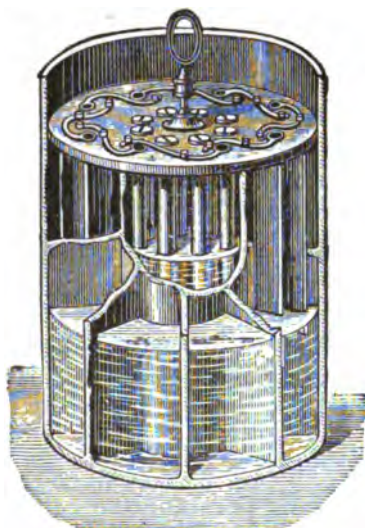

FIG. 47.—ABOILARD CELL.

water 1000 grams, sodium bichromate 200 grams, sulphuric acid 350 grams, hydrochloric acid 30 grams.

Chardin Cautery Cells.—Cell No. 1. A battery of these cells represented in Fig. 48 consists of a vessel of enamelled porcelain divided into two compartments, *A* and *B*, by a horizontal perforated partition. A solution of potassium bichromate is placed in the lower compartment, *B*. The zinc and carbon plates are arranged in the upper compartment, *A*, and connect with platinum terminals. A vertical partition, *C*, forms a small chamber having two openings. One, *E*, serves for the intro-duction of the liquid and is closed by a rubber stopper. The other, *D*, allows escape of gases during the action of the cell. When the battery is placed on its side, *FG*, the liquid runs

FIG. 48.—CHARDIN BATTERY.

out of the chamber B through the holes in the horizontal, but now vertical, partition, and thus comes into contact with the zinc and carbon, thus setting the battery into operation. The partition C prevents the liquid entering the small compartment and so having access to the opening D. When it is desired to throw the pile out of operation, it is returned to its normal position on end.

Cell No. 2. The exterior vessel is divided into tight compartments, of which one, A, receives the zinc, and the other, D, contains the carbon and the bichromate solution. Fig. 49 shows the cell in operation with the zinc in the liquid. When it is desired to disconnect the cell, the zinc is taken out of the compartment D, put into the compartment A, and the latter is thus closed by the stopper B.

FIG. 49.—CHARDIN CELL.

Cell No. 3 (Fig. 50). In the battery formed of these cells the zincs and the carbons F are fastened
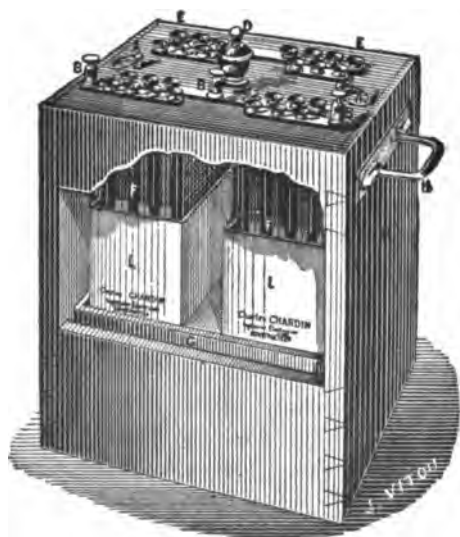

FIG. 50.—CHARDIN BATTERY.

permanently to the under side of the cover by screws, E, and the exciting liquid is placed in a cup or cups, L, which cups rest upon a movable tray, G. When it is desired to set the pile in operation, the tray G and hence the cups are elevated by means of a vertical screw operated by a milled head, D; so that the zincs and carbons are then immersed in the liquid.

Cell No. 4. In the battery of cells of this form, as shown in Fig. 51, the zincs and carbons, C, are supported by coiled springs above the exciting liquid which fills the lower portion of the vessel A. The ends of the spiral springs B extend beneath a pedal, P, which is on the upper end of the supporting rod for the plates. When it is desired to move the plates into the liquid, the pedal is pushed down under and against the action of the spring, which spring lifts the plates out of the liquid again when pressure on the pedal is removed. The rods F are guide-rods for controlling the vertical movement of the plates.
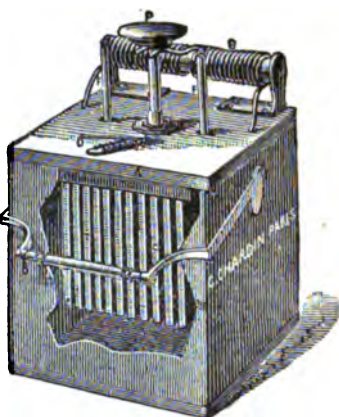

FIG. 51.—CHARDIN BATTERY.

Boisseau du Rocher Cautery Battery.—This battery, as shown in Fig. 52, consists of two superposed vessels, B and C, com-
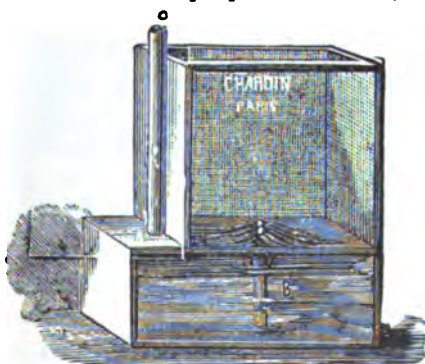

FIG. 52.—BOISSEAU DU ROCHER BATTERY.

municating by a tube which enters the lower vessel, *B*, and contains a solution of sodium bichromate to which sulphuric acid is added. The upper vessel, *C*, contains the zincs and carbons. A rubber bulb is connected with the tube *A*, so that when air is forced into this tube, the liquid is driven up through the tube extending between the vessels, and thus reaches the electrodes. In the more complete form of this
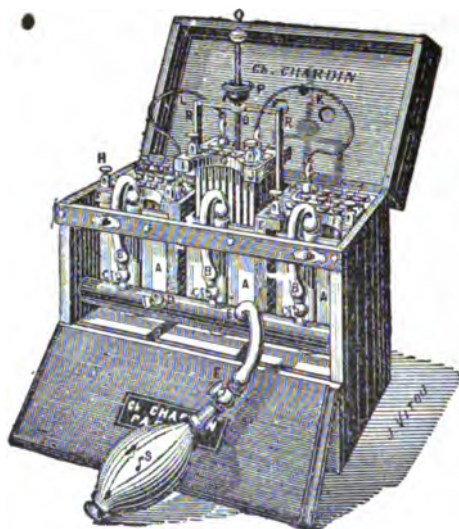

FIG. 53.—BOISSEAU DU ROCHER BATTERY.

battery, shown in Fig. 53, there is the same arrangement already described in connection with the Chardin battery, and also a rubber bulb by means of which the air is forced in in the manner described, so that the entire battery can be set quickly into operation whenever desired.

Trouvé Cautery Battery (1875).—The construction of this battery is shown in Fig. 54. Three plates of carbon are connected together to form the negative electrode. The three corresponding plates of zinc are in rear and are connected together and to three other plates of carbon. Finally the three last plates of zinc are connected to the front and to
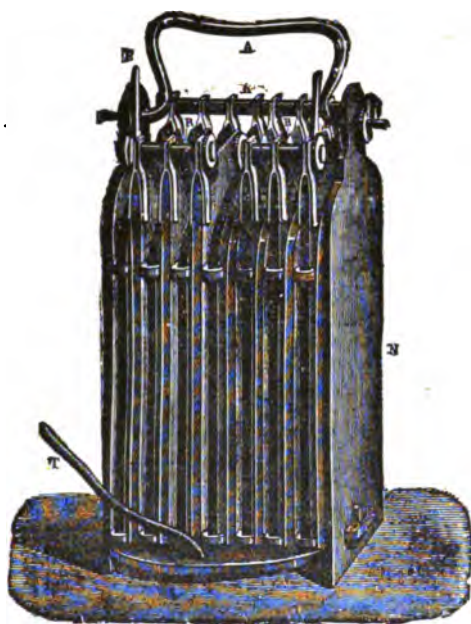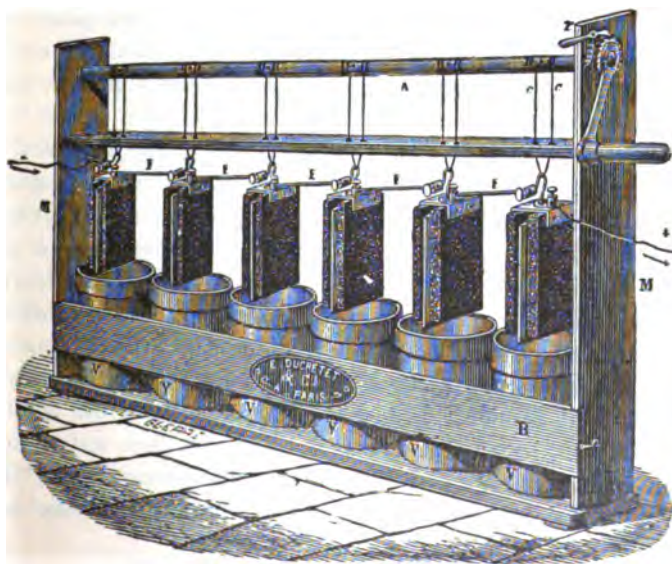
FIG. 54.—TROUVÉ BATTERY.

FIG. 55.—DUCRETET BATTERY.

the left. The electrodes are immersed in a trough containing a solution of potassium bichromate. A tube is provided for injecting air into the lower part of the cell, thus preventing depolarization. A battery weighing 5 kilograms and short-circuited gives, according to d'Arsonval, the following constants: E. M. F., 4 volts; intensity, 118 amperes; resistance, 0.001 ohm.
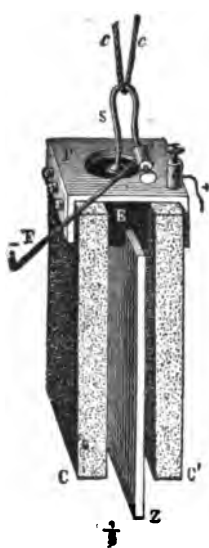

Ducretet Windlass Battery.—Bunsen, Baudet, Ducretet, Gaiffe, Hauck, Jarriant, Stohrer, Tissandier, Trouvé, and others have arranged the zinc electrode of a battery on windlasses by means of which they may be plunged into or withdrawn from the exciting liquid at will. Fig. 55 represents a windlass battery of the Ducretet type, and Fig. 56 shows, on a larger scale, the details of the hook support for the electrodes. In this figure Z is a zinc plate terminated by the hook S, which serves to suspend the electrodes by means of cords, c, and carries a coupler to which is fixed the conductor F. The carbon plates C C' are connected to a piece of metal, P, insulated from the zinc plate by a block of ebonite, E. The piece P carries the binding post which serves as the other terminal of the element.

FIG. 56.
DUCRETET BATTERY.

Trouvé Windlass Battery.—The construction proposed by Trouvé is represented in Fig. 57. His solution is prepared in the following manner: In a vessel of enamelled earthenware containing 12 litres of water (sufficient for a battery of 6 cells) is dissolved 1800 grams of potassium bichromate in powder. After the liquid has been stirred with a glass rod, 2700 grams of sulphuric acid is poured in in a fine stream, the solution being constantly agitated. The liquid thus obtained is clear, and does not crystallize on cooling. E. M. F. = 1.9 to 2 volts. A battery of 6 cells is stated to be capable of furnishing one-half metric horse-power hour. The minimum consumption of zinc is 105 grams, and the maximum

consumption 133 grams, giving an average of 122 grams per cell. The theoretical consumption is 53 grams per cell, or 318 grams for a battery of 6 cells. The consumption in practice
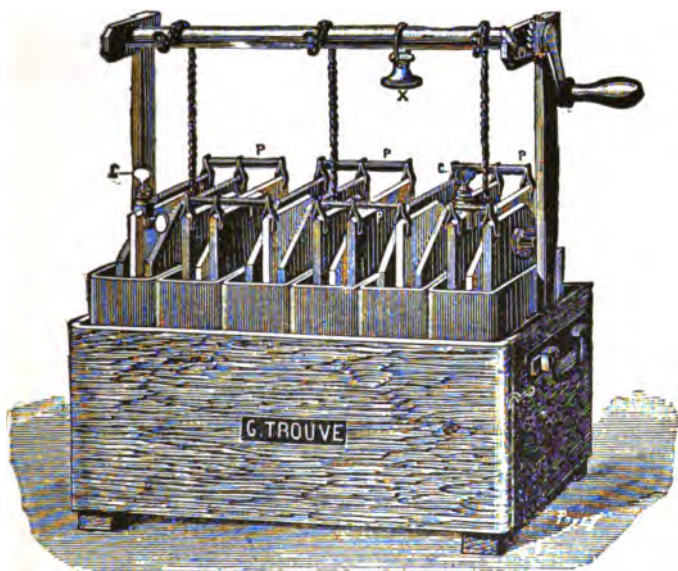

FIG. 57.—TROUVÉ BATTERY.

is represented by the following figures: zinc, 732 grams; potassium bichromate, 1200 grams, sulphuric acid, 3600 grams.

Byrne Cell (1878).—Zinc^{Hg}-platinum and solution composed of water 280 grams, potassium bichromate 35 grams, sulphuric acid 56 grams. The platinum electrode is composed of a sheet of copper covered with a lead plate to which is applied platinum foil. The object of this arrangement is to diminish the resistance of the electrode without increasing the thickness of the platinum plate. This cell is furnished with a rubber bellows intended to blow in air and agitate the liquid, and thus to diminish the effects of polarization. E. M. F. = 1.73 to 1.97 volts.

Carpantier Cell (1885).—This cell has a single bichromated liquid and depends on the following principle: If in a liquid

the two arms of a filled siphon are placed so that the end of the long arm is near to the bottom of the vessel and the short one near to the surface, changes in density of the liquid will determine its circulation. When the two electrodes of the cell are inserted and the current established, the zinc dissolves, increases the density of the liquid, and circulation begins. The liquid charged with zinc descends to the bottom of the vessel, and the fresh liquid rises to the upper part. Each cell should yield 1.5 amperes.

D. Tommasi Cell (1881).—Zinc^{Hg}-carbon, solution of sodium bichromate composed of water 1000 grams, sodium bichromate 300, sulphuric acid 450. E. M. F. = 1.8 to 1.9 volts. A double sulphate of chromium and sodium is here formed.

Chutaux Cell.—The Zinc^{Hg} is embedded in sand, which fills about one half of the vessel, the upper portion of which is packed with carbon surrounded by carbon powder. A layer of sand is placed over all. The exciting liquid is contained in an inverted bottle from which it trickles, drop by drop, and in traversing the cell, escapes by an opening in the bottom. In practice, several of these cells are arranged in a vertical column, so that the liquid flows from one down into the other. The exciting solution consists of water 1500 grams, potassium bichromate 150, mercuric sulphate 50, and sulphuric acid at 66° 200 grams. This liquid gives an electromotive force rather smaller than that of the ordinary bichromate cell, and polarization appears to be reduced.

Partz Cell.—Zinc^{Hg}-carbon and a solution containing zinc chloride 15 parts, ammonium bichromate 15 parts, and water 100 parts. E. M. F. = 1.45 volts.

The chemical reaction is disengagement of hydrogen and ammonia, and formation of a chromo-oxychloride of zinc.

Ponci Cell.—Zinc^{Hg}-carbon, solution composed of potassium bichromate 1 part, water 10 parts, hydrochloric acid 5 parts. The elements of a battery are disposed so that the exciting liquid may circulate from one to the other.

Putot Cell.—Zinc^{Hg}-carbon, solution containing potassium bisulphate 100 grams, chlorochromate of potassium 30 grams,

water 500 grams. The chlorochromate is obtained by melting in a clay crucible 9 parts of potassium chloride and 17 parts of potassium bichromate. This pile has been adopted for military uses for the reason that it does not involve the handling of any acid nor the transport of a solution, since both the bisulphate and the chlorochromate are solid, and the liquid therefore may be produced at any time by simply dissolving them in water.

Delaurier Cell.—Zinc^{Hg}-carbon and solution composed of water 400 grams, potassium bichromate 45, sulphuric acid at 66° 90, sodium sulphate 40, ferrous sulphate 40.

Robert Cell (1886).—Zinc-carbon, solution containing a mixture of potassium permanganate, potassium bichromate, sodium chloride, and ammonium chloride. E. M. F. = 1.8 volts.

Voisin and Drosnier Salt.—This is prepared in the following manner: 100 parts of potassium sulphate are dissolved, hot, in 400 parts of sulphuric acid, and to this is added, in small quantities at a time, 170 parts of pulverized potassium bichromate. When the bichromate is dissolved, the liquid is poured into moulds and allowed to harden, the solid material being afterwards kept in corked bottles. For use, the substance is dissolved in five times its weight of water. This salt appears to be constituted of a mixture of acid sulphate of potassium (SO_4KH) and of a solid combination of sulphuric acid and chromic acid $(CrO_3, 2SO_3)$.

In order to determine whether the bichromate of potassium solution is used up, a few drops of nitrate of silver may be added to a small quantity of it in a test-tube. If the solution contains chromic acid even in small quantity, a red precipitate of silver chromate will appear.

III. VARIOUS CELLS.

Urquhart Cell, represented in Fig. 58, has an arrangement by means of which gravity causes the exciting liquid to continue in motion until it is exhausted. The containing vessel

is cylindrical and deep.   The plates are two disks of carbon
and one of zinc, placed in a horizontal plane, in a wooden case

fitting the containing vessel in the manner of
an air-tight piston.   The piston is packed by
means of a rubber ring, stretched in a groove
turned in the face, as represented in section.
The carbon plates are connected together by
means of a platinum stem, which passes
through an opening in the zinc.   The connec-
tion with the zinc is made by means of a plug
and taper tube of platinum, with a gutta-
percha-covered wire leading out of the cell.
By these means the zinc plate, when worn,
may be replaced by a fresh disk without
trouble.

FIG. 58.—URQUHART
CELL.

The exciting liquid is poured into the upper half of the
containing vessel and flows into the cell through a hole in
the upper carbon.   It escapes through a smaller hole in the
lower carbon plate into the lower compartment, in which there
is a small air-outlet.   By this means it is claimed that the
action of the cell is rendered continuous as long as any of the
exciting fluid remains in the upper compartment.   The internal
resistance is said to be not more than 0.1 ohm.

Case Cell.—This is intended to consume carbon, which is
here the positive electrode.   It is described as follows :

In a glass cell containing sulphuric acid, c. p. sp. gr. 1.81,
temperature 75^c Fahr., two electrodes are immersed, one of
platinum, the other of lump graphite; only a slight E. M. F.
is indicated, 0.007 volt, due to the combination, the graphite
acting as a positive element ; on the addition of a small quan-
tity of potassium chlorate to the acid the E. M. F. immediately
rises to 0.08 volt, the graphite being disintegrated after a time.
The cell polarizes rapidly.   The reaction of potassium chlorate
with sulphuric acid may be represented by the following equa-
tion : $3KClO_3$ (potassium chlorate) $+ 2H_2SO_4$ (sulphuric acid)
$= 2ClO_2$ (peroxide of chlorine) $+ KClO_4$ (potassium perchlo-
rate) $+ 2KHSO_4$ (acid sulphate of potassium) $+ H_2O$ (water).

Chlorine peroxide (ClO₂) appears to be the only active agent. It is decomposed by the carbon, chlorine being evolved with some oxygen. There is probably much waste of energy through local action, as the chemical reactions go on when the circuit is open, but to a less extent. In another experiment an electrolyte was formed of sulphuric acid and chlorine peroxide, the gas being generated in a retort by the action of sulphuric acid on chlorate potassium, and conducted over into the acid in which it was dissolved. With a positive element of graphite opposed to platinum an E. M. F. of 0.7 volt was obtained. This cell appears at the present time to have little practical value on account of the explosive character of the gas generated (explosible at 140° Fahr., and decomposing in sunlight), and also because the cost of the potassium chlorate required renders it, for equal amounts of obtainable energy, about as expensive as the zinc-consuming cell.

Faure's Carbonate of Iron Battery is composed of wooden troughs, about 27 ft. long, by 3 ft. 9 in. high and 6 ft. 6 in. wide, enclosing some hundred or so double electrodes 6 ft. 6 in. wide. These electrodes are constituted of an agglomerate of carbon obtained by grinding up in a mill, drying, and then carbonizing at 1400° C. a paste composed of one quarter by weight of oats, one quarter of bituminous coal, and one half of very porous, clayey earth. An agglomerate is thus obtained which is extremely porous, with which one side of the electrodes only is covered, the other receiving a coating of tar, rendered entirely impermeable by rebaking. The porous side of each electrode is covered with a large piece of netting or coarse sailcloth. The space between the double electrodes is filled in with granulated iron. The liquid used is salt water led in by tubes. The current is taken from two iron plates at the two extremities. The space between one of the plates and the last electrode is filled in with coke or copper turnings of a sufficient conductivity to carry the current of 1000 amperes generated by this battery at a pressure of about 1.15 volts.

The elements of iron and carbon immersed in salt water (NaCl) produce chlorate of iron, caustic soda, and hydrogen,

with an E. M. F. of about 0.30 volt; the hydrogen recombining with the oxygen increases this by 0.40 volt; and the carbonization of the soda by the carbonate of iron adds another 0.30 volt, which is again increased 0.15 volt by the use of reduced porous iron instead of solid iron. Thus the total E. M. F., according to M. Faure, is $0.30 + 0.40 + 0.30 + 0.15 = 1.15$ volts.

In the electrolytic reaction the carbonate of iron and the chlorate of iron form carbonate of iron and chlorate of sodium, which is thus regenerated; the battery only uses the iron transformed into carbonate, which, as will be seen, is easily regenerated, as well as the carbonic acid used for this regeneration. Depolarization is effected by the gases which penetrate between the faces of each double electrode. The reduction of the carbonate of iron takes place in a retort charged with carbonate of iron, and traversed from top to bottom by reducing gases—CO, H, etc.—coming from a gasogene. Passing from the retort, these gases take fire on contact with the air, forming carbonic acid, which passes around the retort to the chimney, whence a portion of the gas is drawn by a pump, which forces it, after washing, into the battery. The air necessary for the combustion of the gasogene arrives, already heated, by a chimney, and the reduced spongy iron passes away cold by a channel placed at the base.

The installation of a Faure primary battery comprises, therefore, besides the battery properly so called (1000 cells), a pump capable of forcing 1000 cubic metres of carbonic acid per hour, a machine to agglomerate the carbonate of iron passed out of the channels, into bricks, and the reducing chamber. According to M. Faure, the consumption of fuel in the retort is not more than 0.3 lb. of coal per pound of iron used in the battery, or per horse-power hour at the battery terminals.

Friedlander's Electric Lamp (Fig. 59).—This is an electric lamp invented by M. A. Friedlander of Berlin. It is composed of a rectangular box of hardened India rubber, divided within into several cells which are formed by parallel walls, also of

India rubber, and moulded with the box. These cells contain the necessary liquid and the electrode plates of the lamp. The carbon plates and the zinc plates are united to an axis of hardened India rubber, so placed as to lower or raise the plates by
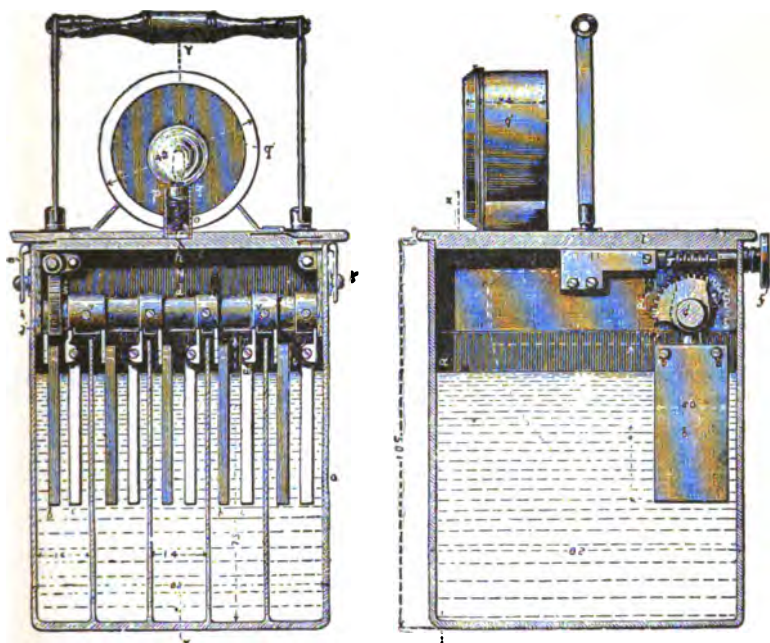

FIG. 59.—FRIEDLANDER'S LAMP.

turning; this movement is produced by means of an endless screw which gears with a toothed sector fixed on to the axis.

The system of immersion of the electrodes is convenient, as it enables them to be partially lowered or raised by simply turning the button, thus regulating the intensity of the light as in an oil or a gas lamp, or extinguishing it completely.

CHAPTER VI.

SINGLE ELECTROLYTE CELLS. *(Continued.)*

IV. PRACTICAL DATA AND TABLES.

E. M. F. AND RESISTANCE OF CERTAIN BICHROMATE CELLS.
(DU MONCEL, 1881.)

		E. M. F.	R.
Water.................... 100 g.	}	2.007 volts.	8.60 ohms.
Bichromate of potassium.. 17 "			
Sulphuric acid .... 22 "			
Water.................... 100 g.	}	1.986 "	9.56 "
Bichromate of potassium.. 10 "			
Sulphuric acid .... 16 "			
Water.................... 100 "	}	1.925 "	8.50 "
Bichromate of potassium.. 6.6 g.			
Sulphuric acid .... 13.33 "			

EFFECT OF THE PERCENTAGE OF SULPHURIC ACID IN THE BICHROMATE SOLUTION ON THE E. M. F. AND RESISTANCE OF THE CELLS. (DU MONCEL, 1881.)

		E. M. F.	R.
Bichromate of potassium.. 10.04 g.	}	2.039 volts.	23.35 ohms.
Water.................... 113 "			
Sulphuric acid........... 60 "			
Bichromate of potassium.. 8.38 g.	}	1.965 "	23 78 "
Water.................... 113 "			
Sulphuric acid..... ...... 30 "			
Bichromate of potassium.. 7.5 g.	}	1.944 "	22.91 "
Water.................... 113 "			
Sulphuric acid........... 30 "			

INFLUENCE OF HEAT ON THE E. M. F. AND RESISTANCE OF THE ELEMENT ZINC^{Hg}-PLATINUM, SOLUTION OF BICHROMATE WITH ADDED SULPHURIC ACID. (W. H. PREECE, 1878.)

Temperature.	E. M. F.	Resistance.
15°.5 C........	2.118 volts........	0.85 ohm.
26 .5 "........	2.118 "	0.77 "
37 .5 "........	2.127 "	0.68 "
44 .5 "........	2.127 "	0.61 "
60 .0 "........	2.127 "	0.54 "
71 .0 "........	2.127 "	0.50 "
82 .0 "........	2.127 "	0 49 "
93 .5 "........	2.127 "	0.45 "

By substituting for the platinum in this cell Byrne's electrode (copper-lead platinum, Preece has obtained the following results:

Temperature.	E. M. F.	Resistance.
26°.5 C......	1.868 volts........	0.78 ohm.
37 .5 "......	2.030 "	0.61 "
44 .4 "......	2 073 "	0.35 "
60 .0 "......	2.127 "	0.24 "
71 .0 "......	2.127 "	0.19 "
82 .0 "......	2.127 "	0.17 "
93 .5 "......	2.127 "	0.14 "

Chemical Reactions of the Bichromate of Potassium Cells.—The ordinary bichromate solution, such as employed in practice, consists of a mixture of potassium sulphate, chromic acid, and sulphuric acid. When zinc is immersed in this solution, the following reactions occur:

1. Decomposition of sulphuric acid with disengagement of hydrogen and formation of zinc sulphate.

2. Reduction, by means of hydrogen, of the chromic acid in chromium oxide.

3. Combination of the chromium oxide with the sulphuric acid (chromic sulphate).

4. Combination of the potassium sulphate with the chromic sulphate (chrome alum).

The action of the zinc on the bichromate solution may be represented by the following equation :

$$3Zn + Cr_2O_7K_2 + 7SO_4H_2 = 3SO_4Zn + (SO_4)_3Cr_2SO_4K_2 + 7H_2O.$$
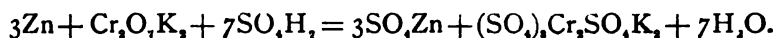
Whence it follows that for 3 molecules of zinc (65 × 3) there must be employed 7 molecules of sulphuric acid (98 × 7) and 1 molecule of potassium bichromate ($Cr_2O_7K_2 = 287$ grams). In order to dissolve, therefore, 1 part by weight of zinc, there is necessary 1.52 of bichromate and 3.5 parts of sulphuric acid.

According to Du Moncel (1881), under the influence of the hydrogen disengaged by reason of the oxidation of the zinc, the sesquioxide of chromium of the chromium sulphate entering into the alum becomes deoxidized and passes to the state of protoxide. There is consequently no longer formed chrome alum, but a double sulphate of potash and of protoxide of chromium. This is indicated by the blue color which the solution assumes after a certain period of closed circuit ; but the salt partially returns to the state of chrome alum under the influence of the oxygen of the air dissolved in the water. At the same time apart of the sulphuric acid of the decomposed chromium sulphate reacts on the zinc oxide in order to form a sulphate or subsulphate of zinc. The same effect is undoubtedly produced on sulphate of potassium, for it appears in the Selmi sulphate of potassium cell that quite an energetic electric development results from the reduction of this salt by zinc oxide due to the decomposition of the water, and that potash is deposited.

TABLES OF E. M. F.'S OF CELLS HAVING A SINGLE
ELECTROLYTE.

E. M. F. OF CERTAIN CELLS USING DILUTE SULPHURIC
ACID. (BECQUEREL.)

	Value of E. M. F. in Open Circuit.
Zinc^{Hg}-zinc	0.04 volt.
Potassium-zinc	1.12 "
Zinc-gold.	1.54 "
" platinum.	1.54 "
" carbon.	1.54 "
" silver	1.05 "
" copper.	1.00 "
" antimony	1.00 "
" bismuth.	0.97 "
" cobalt	0.86 "
" nickel.	0.85 "
" aluminium	0.75 "
" iron	0.60 "
" tin	0.52 "
" lead	0.52 "
" cadmium.	0.32 "

According to D. Tommasi, the E. M. F. of the zinc-platinum
couple is much lower than that of the zinc-carbon couple.

E. M. F.'S PRODUCED BY CERTAIN METALS AND ALLOYS ON
CONTACT WITH SEA-WATER. (BECQUEREL.)

Metals.	E. M. F. (that of zinc being 100).
Zinc	100.0
Zincked iron	95.5
Soft iron	65.4
Sheet iron	64.0
Lead	53.3
Red copper	30.9
Alloys of Zinc and Copper.	
Zinc	100.0
Copper	31.9

COMPOSITION OF ALLOYS.

Zinc.	Copper.	E. M. F. (that of zinc being 100).
77.7	22.2	96.9
67.9	31.4	90.3
70.0	30.0	75.0
64.9	35.1	42.0
60.4	39.6	37.0
59.0	50.0	35.4
54.2	45.8	35.0
45.7	54.3	32.4

Alloys of Zinc and Lead.

Lead			53.3

Zinc.	Lead.	Copper.	
50.0	50.0	—	100.0
33.3	66.6	—	92.5
20.0	80.0	—	92.5
60.0	20.0	30.	35.4

Inversion of the Current in Cells.—If a copper-silver couple be placed in a solution of potassium sulphite, the following facts are observed :

1. The copper is attacked first, and consequently the current appears to move from the copper to the silver.

2. At the end of a short time the current ceases, the silver becomes covered with sulphur, and this chemical reaction produces a current turned in the opposite direction to that of the original current, and at the same time the layer of sulphur which has been formed on the copper dissolves.

3. Finally the copper is attacked anew, the current changes direction again, and these inversions are repeated many times. (Faraday.)

If the couple be formed of copper-iron, the pole which is found on the copper side in salt or acidulated water, or in a potash solution, appears on the iron side when the couple is plunged in ammonia. In a couple formed of lead and copper the pole which is on the lead side in dilute nitric acid is on the copper side in the same acid concentrated. (De la Rive.)

TABLE SHOWING THE DIRECTION OF CURRENT OCCURRING IN A GIVEN CELL, DEPENDING UPON THE EXCITING LIQUID EMPLOYED. (FARADAY.)

Dilute Nitric Acid.	Dilute Sulphuric Acid.	Hydrochloric Acid.	Nitric Acid.	Solution of Potash.	Sulphydrate of Potassium (colorless)	Sulphydrate of Potassium (yellow).
1 Silver	1 Silver	3 Antimony	5 Nickel	1 Silver	6 Iron	6 Iron
2 Copper	2 Copper	1 Silver	1 Silver	5 Nickel	5 Nickel	5 Nickel
3 Antimony	3 Antimony	5 Nickel	3 Antimony	2 Copper	4 Bismuth	4 Bismuth
4 Bismuth	4 Bismuth	4 Bismuth	2 Copper	6 Iron	8 Lead	3 Antimony
5 Nickel	5 Nickel	2 Copper	4 Bismuth	4 Bismuth	1 Silver	8 Lead
6 Iron	6 Iron	6 Iron	6 Iron	8 Lead	3 Antimony	1 Silver
7 Tin	8 Lead	8 Lead	7 Tin	3 Antimony	7 Tin	7 Tin
8 Lead	7 Tin	7 Tin	8 Lead	9 Cadmium	2 Copper	9 Cadmium
9 Cadmium	9 Cadmium	9 Cadmium	10 Zinc	7 Tin	10 Zinc	2 Copper
10 Zinc	10 Zinc	10 Zinc	9 Cadmium	10 Zinc	9 Cadmium	10 Zinc

The number adjacent to the name of each metal indicates the order of the current if the liquid used is a dilute acid; the direction of the current being always such that it is determined by the metal which follows forming a couple with the one which precedes. The following metal therefore forms the positive electrode.

E. M. F.'S OF THE MAGNESIUM-PLATINUM COUPLE IM-
MERSED IN DIFFERENT LIQUIDS. (G. GORE, 1885.)

Solutions.	E. M. F.'s.	
	Temp. 15°.6.	Temp. 71°.1.
Sulphuric acid.........	1.92 volts.	
Formic "	1.84 "	2.08 volts.
Oxalic "	1.73 "	1.88 "
Tartaric "	1.68 "	1.84 "
Chloride of potassium..	1.44 "	1.53 "
Bromide of " ..	1.67 "	1.75 "
Iodide of " ..	1.58 "	1.44 "
Cyanide of " ..	1.48 "	
Chlorate of " ..	1.73 "	2.13 "
Sulphate of " ..	1.50 "	1.48 "
Chloride of sodium.....	1.50 "	1.53 "
Sulphate of magnesium.	1.75 "	1.64 "
Potassium alum........	1.81 "	1.73 "
Ammonium alum......	1.70 "	1.84 "

E. M. F. OF CERTAIN COUPLES USING DILUTE SULPHURIC
ACID. (POGGENDORFF, 1845.)

Sulphuric acid, 1 part ; water, 49 parts.

Zinc-tin...........................	0.441 volt.
Tin-copper.......................	0.442 "
Zinc-copper......................	0.890 "
Iron-copper......................	0.440 "
Zinc-silver	1.137 "
" cadmium....................	0.366 "
Cadmium-iron....................	0.206 "
Zinc^{Hg}-iron........................	0.580 "
" tin........................	0.573 "

*Nitric acid (1.22 specific weight of water) with 9 times its weight
of water.*

Zinc^{Hg}-copper....................	0.882 volt.
" platinum...................	1.495 "
Copper platinum.................	0.616 "

Hydrochloric acid (density = 1.113), 1 *part; water,* 9 *part*

Zinc^{Hg}-copper .... 0.788 volt.
" platinum .... 1.537 "
Copper-platinum .... 0.743 "
Silver-platinum .... 0.620 "

Potash, 1 *part; water,* 6 *parts.*

Zinc-iron .... 1.003 volts.
" silver .... 1.198 "
" platinum .... 1.257 "
" antimony .... 0.541 "

Carbonate of potash, concentrated solution.

Zinc-iron .... 0.832 volt.
" copper .... 0.909 "
" platinum .... 1.078 "
Iron-copper .... 0.077 "

Chloride of potassium, concentrated solution.

Zinc-iron .... 0.476 volt.
" copper .... 0.743 "
" platinum .... 1.346 "
Iron-copper .... 0.260 "

Bichromate of potassium, 3 *parts ; sulphuric acid,* 4 *parts ; water,*
18 *parts.*

Zinc-copper .... 0.961 volt.
" carbon .... 1.574 "
" platinum .... 0.977 "

E. M. F. OF CERTAIN DILUTE SULPHURIC ACID COUPLES.
(POGGENDORFF AND BECQUEREL).

	On Open Circuit.	After Polarization.
Zinc-silver.	1.03 volt.	——
Zinc^{Hg}-copper	0.94 "	0.44 volt.
" silver	1.24 "	0.52 "
" platinum	1.44 "	0.65 "

According to D. Tommasi, the E. M. F. of the zinc-platinum couple is much below that of the zinc-carbon couple (1.37 maximum value ; 0.85 minimum value).

In general, the electromotive force of any couple is greater as the volume of air condensed by the inactive electrode augments.

E. M. F.'S DUE TO THE ACTION OF LIQUIDS ON METALS.
(E. BECQUEREL, 1855.)

For this determination Becquerel uses two porous cups placed in a containing vessel. One is filled with nitric acid, and the other with a solution which should react on the oxidizable metal. The external vessel contains the same solution. There is thus obtained a couple yielding a constant current in which the negative plate is unceasingly depolarized by its contact with nitric acid. There is first determined the electric effect resulting from the mutual action of the two liquids, and the number thus obtained is subtracted from that which expresses the effect of the couple. The difference gives the E. M. F. produced when the metal is alone attacked.

Metals.	Composition of the Liquid.		
	Sulphuric Acid... 1 Water............ 9	Hydrochloric Acid 1 Water..... 10	Potash...... ... 1 Water. 4
	volts.	volts.	volts.
Amalgam of potassium (1%).................	2.334	....	....
Zinc (amalgamated).....	1.389	1.406	1.377
Zinc (pure).	1.347	1.392	1.326
Cadmium	1.066	1.134	0.950
Lead.......	0.896	0.905	0.850
Tin....................	0.888	0.913	1.143
Iron.......	0.828	0.845	0.850 ?
Aluminium...........	0.692	1.134	1.445
Nickel............. ...	0.607	0.658	0.408
Cobalt.	0.590	0.641	0.527
Bismuth...............	0.498	0.561	0.612
Antimony.............	0.473	0.488	0.819 ?
Copper............	0.473	0.624	0.561
Silver..................	0.293	0.643	0.000
Mercury.	0.425	....	....
Gold..................	0.000	....	....
Platinum......	0.000	....	0.170 ?

At the outset, iron, nickel, and cobalt give a well-marked action ; but as soon as the current starts there is a diminution of intensity, and the metals act as if they were less attacked and had become inactive like passive iron. This effect is eliminated by plunging the metals in a weak solution of sulphuric acid.

Zinc and lead, however, with nearly all liquids, maintain nearly the same ratio of electromotive force.

When the electromotive force of a simple couple formed of two metals placed in one of the preceding liquids is desired, the difference of the E. M. F.'s of both of them is to be taken. Thus, with zinc-platinum and zinc-copper couples, using dilute sulphuric acid, we have

Zinc-platinum.......... $1.347 - 0.000 = 1.347$
Zinc-copper. .... $1.347 - 0.473 = 0.874$

MAXIMA AND MINIMA E. M. F.'S OF CERTAIN SINGLE ELECTRO-LYTE COUPLES (E. REYNIER).

Reynier has measured these two extreme values by means of two forms of his cells especially adapted for the purpose which he calls " maxima" and " minima" cells. In the first of these two forms the negative electrode is 300 times greater than that of the positive. In the second, on the other hand, the negative electrode is very small and the E. M. F. is determined after long standing and short circuit.

Exciting liquid. .. { *Water*.................... 1000 c. cm.
{ *Monohydrated sulphuric acid*. 2 "

	Maxima.	Minima.
Zinc-platinum........	....	0.5 volt.
" iridium..........	....	0.270 "
" gold.	....	<0.156 "
" silver...........	....	<0.098 "
" carbon.	1.22 volt.	0.04 "
" lead....	0.55 "	0.144 "
" copper.	0.94 "	0.194 "
" iron.............	0.429 "	0.309 "

THE VOLTAIC CELL.

	Maxima.	Minima.
Zinc^{Hg}-platinum......	....	0.561 volt.
" silver........	....	0.108 "
" carbon........	1.26 **volt.**	0.226 "
" lead........	0.684 "	0.152 "
" copper........	1.072 "	0.272 "
" iron.........	0.476 "	0.323 "
" zinc.........	....	0.09 "
Iron-copper.........	0.50 "	....

Exciting liquid.. { Water...................... 1000 grams.
Chloride of sodium........... 250 "

	Maxima.	Minima.
Zinc-platinum........	....	0.034 volt.
" iridium........	....	0.052 "
" gold.........	,...	< 0.028 "
" carbon.........	1.08 volt.	< 0.040 "
" silver...........	....	0.043 "
" copper.........	0.78 "	0.025 "
" iron...........	0.378 "	0.046 "
" lead...........	0.503 "	0.044 "
Zinc^{Hg}-copper........	0.82 "	....
" " iron.....	0.469 "	....
" " lead.....	0.52 "	....
Iron-copper........	0.26 "	....
Lead-copper.........	0.26 "	....

Exciting liquid.. { Water...................... 1000 grams.
Chloride of zinc.............. 110 "

	Maxima.	Minima.
Zinc copper...........	0.85 volt.	....
Zinc^{Hg}-copper........	0.86 "	....

Exciting liquid.. { Water...................... 1000 grams.
Sulphate of zinc............. 500 "

	Maxima.	Minima.
Zinc-copper..........	0.998 volt.	....
Zinc^{Hg}-copper........	1.04 "	....

Exciting liquid.. { Water..................... 1000 grams.
Sulphuric acid............... 60 "

	Intial E. M. F.	E. M. F. after Several Minutes.	E. M. F. after Several Hours.
Zinc (distilled) carbon..	1.37 volts.	1.0 volt.	0.83 volt.

E. M. F.'S OF SEVERAL VOLTAIC COMBINATIONS HAVING THE POSITIVE ELECTRODE ENCLOSED. (E. REYNIER).

	New.	Polarized.
Ordinary zinc enclosed, exposed copper and dilute sulphuric acid.....	0.848 volt.	0.441 volt.
Ordinary zinc enclosed, exposed iron and dilute sulphuric acid.........	0.401 "	0.409 "
Amalgamated zinc enclosed, exposed iron and dilute sulphuric acid....	0.466 "	0.466 "
Amalgamated zinc enclosed, exposed iron, 20% sol. of sodium bisulphate.	0.504 "	0.509 "

E. M. F.'S OF PLATINUM AND HYDROGENIZED PALLADIUM.

Zinc^{Hg}-platinum, dilute sulphuric acid...... 0.513 volt (about)..
Zinc^{Hg}-palladium, " " " ...... 0.365 " "

E. M. F.'S OF CERTAIN VOLTAIC COUPLES IMMERSED IN A MIXTURE OF 5 PARTS NITRIC ACID AND 11 PARTS WATER. (G. GORE, 1885.)

Zinc-cadmium.................	0.2131 volt.
" lead....................	0.3901 "
" tin.....................	0.4301 "
" iron...................	0.4867 "
" aluminium	0.5057 "
" nickel..................	0.8571 "
" copper.............	0.8970 "
" silver..................	1.1490 "
" palladium...............	1.1828 "
" gold....................	1.4150 "
" platinum................	1.4293 "
Cadmium-platinum.............	1.2162 "
Lead "	1.0392 "
Tin "	0.9992 "
Iron "	0.9426 "
Aluminium "	0.9236 "
Nickel "	0.5722 "
Copper "	0.5223 "
Silver "	0.2803 "

Ê. M. F. OF SINGLE-LIQUID CELLS. (B. C. DAMIEN, 1885.)

TABLE I.—CELLS OF ZINC, COPPER, AND DIFFERENT SALINE SOLUTIONS.

Nature of the Solution.	Density at 15°C.	Composition. Centesim.	o.	B. M. F.'s after a number of days equal to								
				5.	12.	26.	40.	91.	155.	191.	290.	340.
			volts.	volts.	volts.	volts.	volts.	volts.	volts.	volts.	volts.	volts.
Sulphate of potash........	1.036	4.5 *	1.035	0.920	0.889	0.842	0.813	0.761	0.721	0.635	0.629	0.602
" " soda........	1.038	10 *	1.012	0.938	0.907	0.903	0.890	0.840	0.761	0.653	0.512	0.404
" " ammonia........	1.075	13.1	1.012	0.838	0.632‡							
" " magnesia........	1.035	5.8*	1.047	1.064	1.047	1.053	1.061	1.058	1.056	1.058	1.063	1.051
" " alumina........	1.135	....	1.050	1.037	1.011†							
" " zinc........	1.064	9.2*	1.004	1.024	1.018	0.970	0.945	0.940	0.945	0.970	0.976	0.962
Nitrate of potash........	1.061	10	0.717	0.691	0.670	0.627	0.576	0.570	9.560	0.565	0.529	0.518
" " soda........	1.183	25	0.666	0.664	0.656	0.599	0.585	0.580	0.589	0.604	0.579	0.562
" " ammonia........	1.081	14.7	0.700	0.362†	0.700	0.600	0.633	0.660	0.602	0.584	0.611	0.597
" " baryta........	1.028	3.3	0.725	0.710	0.723	0.686	0.669	0.630	0.600	0.557	0.528	0.517
" " strontium........	1.088	10	0.745	0.750								
Carbonate of potash........	1.061	6.8	0.203	0.088	0.074	0.056	0.050	0.039	0.031	0.021	0.020	0.018
" " soda........	1.046	11	0.214	0.140	0.080	0.070	0.061	0.058	0.051	0.048	0.040	0.032
Chloride of potassium........	1.077	12	0.788	0.916	0.921	0.883	0.801	0.805	0.771	0.797	0.794	0.781
" " sodium........	1.061	8.5	0.805	0.914	0.915	0.895	0.840	0.723	0.614	0.578	0.571	0.532
" " ammonium........	1.039	13	0.845	0.853†	0.811	0.884	0.927	0.902	0.853	0.788	0.802	0.767
" " barium	1.110	12	0.782	0.803	0.682	0.683	0.675	0.683	0.676	0.680	0.702	0.673
" " calcium........	1.212	23	0.743	0.673	0.785	0.740	0.744	0.683	0.325	0.147	0.225	0.302
" " zinc........	1.384	37.5	0.746	0.750	0.437‡							
Iodide of potassium........	1.169	20	0.591	0.579	0.860	0.841	0.819	0.782	0.603	0.641	0.702	0.653
Bromide of potassium........	1.112	14.5	0.735	0.863	0.673	0.558	0.369	0.380	0.403	0.427	0.488	0.433
Water (pure)........	....	....	0.916	0.737	0.749	0.653	0.609	0.604	0.680	0.676	0.643	0.625
Water (ordinary)........	....	....	0.811	0.802								

* The asterisks indicate a composition approaching a hydrated salt.

† Roughened copper.   ‡ Abundant deposit on the zinc.

E. M. F. OF SINGLE-LIQUID CELLS. (B. C. DAMIEN, 1885.)

TABLE II.—CELLS OF LEAD, PLATINUM, AND DIFFERENT SALINE SOLUTIONS.

Nature of the Solution.	Density at 15°C.	Composition. Centesim.	B. M. F.'s after a number of days equal to									
			0.	19.	33.	54.	69.	95.	121.	230.	360.	310.
			volt.	volt.	volt.	volt.	volt.	volt.	volt.	volt.	volt.	volt.
Sulphate of potash	1.036	4.5	0.555	0.474	0.419	0.495	0.487	0.449	0.440	0.548	0.436	0.425
" soda	1.038	10*	0.489	0.437	0.425	0.394	0.375	0.372	0.365	0.455	0.414	0.391
" ammonia	1.075	13.1	0.455	0.256	0.250	0.203	0.222	0.218	0.206	0.348	0.321	0.297
" magnesia	1.035	5.8*	0.537	0.437	0.449	0.566	0.602	0.650	0.643	0.683	0.692	0.599
" alumina	1.035	...	0.317	0.244	0.255	0.252	0.242	0.227	0.203	0.181	0.178	0.162
" zinc	1.064	9.2*	0.514	0.306	0.216	0.232	0.227	0.233	0.219	0.215	0.209	0.200†
" copper	1.079	12.1*	0.270	0.188	0.166	0.171	0.196	0.205	0.237	0.286	0.209	0.201†
Sulphuric acid, concentr	1.792	85.8*	0.800	0.425	0.427	0.329	0.470	0.480	0.540	0.675	0.591	0.547
Bisulphate of soda	1.304	...	0.333	0.237	0.222	0.216	0.242	0.237	0.226	0.263	0.241	0.227
Nitrate of potash	1.061	10	0.621	0.552	0.578	0.600	0.580	0.572	0.580	0.660	0.579	0.575
" soda	1.183	25	0.575	0.583	0.614	0.623	0.602	0.579	0.547	0.535	0.521	0.502†
" ammonia	1.081	14.7	0.615	0.620	0.601	0.594	0.590	0.582	0.571	0.586	0.573	0.563
" baryta	1.028	3.3	0.510	0.520	0.593	0.626	0.620	0.603	0.609	0.611	0.602	0.587
" strontia	1.088	10	0.618	0.606	0.654	0.620	0.618	0.607	0.577	0.538	0.526	0.517†
" lead	1.293	18.3	0.670	0.718	0.679	0.618	0.642	0.657	0.675	0.721	0.691	0.653
Carbonate of potash	1.061	6.8	0.603	0.542	0.601	0.588	0.591	0.575	0.555	0.543	0.532	0.521
" soda	1.046	11	0.573	0.572	0.583	0.598	0.593	0.582	0.566	0.552	0.547	0.533
Arseniate of soda	1.022	5.3*	0.587	0.443	0.462	0.436	0.417	0.452	0.421	0.441	0.419	0.409

* The asterisks indicate a composition approaching a hydrated salt,

† Deposit on the lead.

E. M. F. OF SINGLE-LIQUID CELLS. (B. C. DAMIEN, 1885.)

TABLE II (Continued).—CELLS OF LEAD, PLATINUM, AND DIFFERENT SALINE SOLUTIONS.

Nature of the Solution.	Density at 15°C.	Composition Centesim.	E. M. F.'s after a number of days equal to									
			0.	19.	33.	54.	69.	95.	121.	220.	260.	310.
			volt.	volt.	volt.	volt.	volt.	volt.	volt.	volt.	volt.	volt.
Chloride of potassium......	1.077	12	0.673	0.437	0.254	0.305	0.309	0.295	0.331	0.430	0.406	0.401
" " sodium	1.061	8.5	0.637	0.357	0.385	0.404	0.422	0.401	0.397	0.501	0.430	0.409
" " ammonium...	1.039	13	0.627	0.242	0.341	0.362	0.357	0.342	0.327	0.313	0.302	0.318
" " barium...	1.110	12	0.591	0.496	0.462	0.526	0.496	0.502	0.526	0.542	0.523	0.511
" " calcium...	1.212	23	0.834	0.623	0.680	0.615	0.623	0.617	0.609	0.609	0.602	0.597
" " zinc...	1.384	37.5	0.727	0.735	0.778	0.838	0.821	0.801	0.743	0.673	0.621	0.606
Iodide of potassium...	1.169	20	0.659	0.491	0.512	0.627	0.632	0.625	0.647	0.715	0.690	0.682
Bromide of potassium...	1.112	14.5	0.550	0.220	0.230	0.254	0.260	0.253	0.282	0.310	0.277	0.269
Chlorate of sodium ...	1.128	20.2	0.686	0.691	0.580	0.582	0.577	0.601	0.582	0.612	0.594	0.577†
" " potassium...	1.018	3.3	0.614	0.570	0.571	0.609	0.618	0.602	0.593	0.556	0.542	0.531
Basic phosphate of soda...	1.033	7.5*	0.546	0.587	0.588	0.620	0.635	0.637	0.629	0.661	0.642	0.637
Ordinary phosphate of soda.	1.019	4.65*	0.591	0.494	0.471	0.488	0.480	0.462	0.403	0.375	0.417	0.401
Salt of phosphorus...	1.044	....	0.485	0.399	0.422	0.409	0.397	0.407	0.402	0.422	0.395	0.382
Pyrophosphate of soda...	1.039	....	0.752	0.670	0.674	0.603	0.592	0.540	0.501	0.422	0.487	0.435
Acetate of sodium...	1.059	11.2	0.684	0.655	0.681	0.679	0.662	0.665	0.653	0.635	0.626	0.617
Borax...	1.008	....	0.575	0.475	0.509	0.499	0.487	0.472	0.468	0.460	0.451	0.441
Silicate of potassium...	1.314	....	0.766	0.657	0.709	0.722	0.725	0.719	0.692	0.601	0.575	0.591
Ordinary water...	....	....	0.579	0.560	0.560	0.591	0.560	0.542	0.519	0.524	0.508	0.501‡

* The asterisks indicate a composition approaching hydrated salt.

† Deposit on the lead.   ‡ Crystallized deposit at the bottom of the jar.

TABLE III.

(B. C. DAMIEN.)

The saline solutions are the same as in the preceding experiments, and the measurements are invariably taken a few hours after the setting up of the cells.

	Zinc.	
	Ordinary.	Amalgamated.
	volts.	volts.
Water (pure) (copper)...............	0.916	0.928
" slightly acidulated (lead)....	0.547	0.629
" " " (iron) ...	0.432	0.482
Sulphate of potash (copper)......	1.035	1.067
" " soda "	1.012	1.037
" " ammonia "	1.012	1.019
" " magnesia "	1.047	1.059
" " aluminium "	1.050	1.062
" " zinc "	1.004	1.047
Nitrate of potash "	0.717	0.757
" " soda "	0.666	0.702
" " ammonia "	0.700	0.723
" " baryta "	0.725	0.728
" " strontia "	0.745	0.757
Carbonate of potash "	0.203	0.252
" " soda "	0.214	0.257
Chloride of potassium "	0.788	0.802
" " sodium "	0.805	0.810
" " ammonia "	0.845	0.850
" " barium "	0.782	0.820
" " calcium "	0.743	0.741
" " zinc "	0.746	0.752
Iodide of potassium "	0.591	0.612
Bromide of potassium "	0.735	0.752

INFLUENCE OF TIME ON THE E. M. F. OF A ZINC-COPPER-SPRING-WATER CELL.

	Zinc.	
	Amalgamated. volts.	Ordinary. volts.
After 2 hours.................	0.928	0.811
" 5 days.................	0.848	0.802
" 12 "	0.792	0.749
" 26 "	0.660	0.653
" 40 "	0.582	0.609
" 91 "	0.489	0.604
" 155 "	0.499	0.680
" 191 "	0.329	0.676
" 290 "	0.302	0.643
" 340 "	0.273	0.625

THE ZINC-COPPER AND MAGNESIUM-SULPHATE CELL.

(B. C. DAMIEN, 1885.)

EFFECT OF CONCENTRATION OF THE SOLUTION.

Solutions.	Density at 15°.	SO_4Mg per cent.	E. M. F.
1	1.010	1.2	1.048 volts.
2	1.035	3.1	1.052 "
3	1.151	14.1	1.050 "
4	1.200	18.2	1.063 "
5	1.247	21.9	1.047 "
6	1.288	25.0	1.043 "

EFFECT OF TEMPERATURE.

For temperatures ranging between 6° and 35° the E. M. F.'s have remained nearly the same, 1.052 to 1.068 volts.

EFFECT OF CLOSING THE CIRCUIT.

Duration of Closing Circuit.	E. M. F.
0 minute....................	1.059 volts.
1 "	0.898 "
5 "	0.825 "
1 hour......................	0.750 "
5 "	0.723 "
12 "	0.715 "

EFFECT OF THE CONCENTRATION OF ALKALINE SOLUTIONS
ON THE E. M. F. OF THE ZINC^{Hg}-PLATINUM COUPLE.
(B. C. DAMIEN, 1885.)

SODA SOLUTIONS.

Density at 15°.	NaHO per cent.	E. M. F.
1.249	23.5	1.342 volts.
1.177	16	1.325 "
1.138	12	1.321 "
1.096	8	1.297 "
1.052	4.9	1.308 "
1.032	3	1.282 "
1.020	2	1.287 "
1	0	1.083 "

POTASH SOLUTIONS.

Density at 15°.	KHO per cent.	E. M. F.
1.230	2.5	1.390 volts.
1.182	19.8	1.380 "
1.143	17	1.381 "
1.100	13	1.368 "
1.074	10	1.358 "
1.051	6.8	1.349 "
1.035	4.5	1.344 "
1.022	3	1.352 "
1.013	1.8	1.321 "
1.002	0.2	1.282 "
1	0	1.083 "

EFFECT OF THE CONCENTRATION OF THE SULPHURIC ACID
ON THE E. M. F. OF THE ZINC^{Hg}-PLATINUM CELL.
(B. C. DAMIEN, 1885.)

Density at 15°.	SO$_4$H$_2$ per cent.	E. M. F.
1.831	92	1.264 volts.
1.670	74.5	1.275 "
1.493	59.3	1.291 "
1.332	43	1.302 "

Density at 15°.	SO₄H₂ per cent.	E. M. F.
1.223	30	1.345 volts, maximum.
1.151	19 8	1.322 "
1.113	15.8	1.275 "
1.065	9.5	1.265 "
1.023	3.7	1.245 "
1	0	1.083 "

E. M. F. of Amalgamated Metals (J. Regnauld, 1861). —1. When there is produced a reduction of temperature during the combination of the metal with mercury, and hence the heat of constitution of the amalgam is greater than that of the metal, the latter rises in the order of positive affinities.

The metals which become electro-positive on alloying with mercury are the following: iron, nickel, cobalt, zinc, tin, antimony, copper, lead, and bismuth.

Zinc, tin, and lead, among these, are the only ones which combine with mercury by simple contact and without auxiliary chemical or physical action.

2. In the case when the inverse conditions apply, that is to say, when there is a disengagement of heat during the formation of the amalgam, the amalgamated metal becomes electro-negative in relation to the free metal.

The metals which become electro-negative on alloying with mercury are the following: potassium, sodium, cadmium, and thallium.

Amalgamated aluminium is more oxidizable than ordinary aluminium.

E. M. F.'S OF AMALGAMS IN WATER CONTAINING 10% SUL-
PHURIC ACID. (E. BECQUEREL, 1855.)

	volts.
Pure cast zinc	1.350
Distilled mercury	0.425
Amalgamated zinc (without excess of mercury)	1.384
" " (another experiment)	1.401
" " (with excess of mercury)	1.415

volts.

Amalgam of zinc, pasty (1 zinc, 10 mercury)............ 1.366
"   "   " liquid (1 zinc, 20 mercury)............ 1.360
"   "   "   " (1 zinc, 30 mercury)............ 1.360
"   " manganese, pasty....................... 1.480
"   "   "   liquid........................ 1.485
"   " ammonium, pasty...................... 2.029
"   " barium, pasty......................... 2.091
"   "   " liquid (with addition of mercury).. 2.012
"   " calcium, pasty......................... 2.162
"   " sodium, pasty (1 sodium, 50 mercury)...... 2.334
"   "   " liquid (1 sodium, 100 mercury).... 2.321
"   "   " liquid (1 sodium, 200 mercury).... 2.303
"   " potassium (1 potassium, 100 mercury) 2.341
"   "   " (1 potassium, 200 mercury) 2.341
"   "   " (1 potassium, 400 mercury) 2.317

E. M. F. OF AMALGAMS OF POTASSIUM AND ZINC.
(WHEATSTONE.)

(The amalgams are contained in porous cups.)

E. M. F.

Amalgam of potassium :   volts.

Solution of sulphate of zinc, zinc.................. 1.043
Solution of sulphate of copper, copper............. 1.122
Solution of chloride of platinum, platinum......... 2.482
Dilute sulphuric acid, peroxide of lead............ 3.525
Dilute sulphuric acid, peroxide of manganese....... 2.921

Amalgam of zinc :

Solution of sulphate of copper, copper............. 1.079
Solution of nitrate of copper, copper.............. 1.043
Solution of chloride of platinum, platinum......... 1.438
Dilute sulphuric acid, peroxide of lead 2.446
Dilute sulphuric acid, peroxide of manganese....... 1.942

E. M. F. OF AMALGAMS.   (C. HOCKIN AND H. A. TAYLOR, 1879.)

I.

Exciting liquid : Solution of 1 *part sulphuric acid* $(D. = 1.838)$ *and* 19 *parts of water.*

Voltaic couple : Zinc^{Hg}—M (metal) (1).

	Pure Metal.	Amalgamated Metal.	Solid Amalgam with Excess of Mercury.	Mercury containing Traces of Metal.
	volt.	volt.	volt.	volt.
Zinc......................	0.043	0.000	0.000	0.029 to 0.253
Cadmium	0.401	0.439	.....	0.488
Tin.................	0.571	0.599	0.596	0.626
Lead....................	0.559	0.627	0.542	0.627
Iron (2).................	0.487	.....	.....	.....
Copper..................	1.052	1.092	1.058	1.084
Silver (3)................	1.326	1.335	0.971	1.363
Gold.....................	1.340	.....	.....	.....
Platinum (4)....	1.477	1.363	1.168	1.086
Copper and lead (6)........	0.608	0.550	.....	.....
Copper and lead (7)........	0.682 to 0.989	0.546	.....	.....
Silver and zinc (8)........	1.004	0.100	.....	.....
Gold and silver (9)........	1.133 to 1.204	1.172	.....	.....
Gold and silver (10).......	1.260 to 1.210	1.088 to 1.220	.....	.....
Gold and silver (11).......	0.882 to 1.067	1.061 to 1.170	.....	.....
Iron and tin..............	0.537	0.543	.....	.....
Platinum and tin..........	0.548	0.552	.....	.....
Lead and zinc.............	0.018	0.000	.....	.....
Silver and copper (12).....	1.070	1.047	.....	.....
Copper and cadmium......	0.730	0.745	.....	.....
Mercury..................	1.363	.....	.....	.....

II.

Exciting liquid: Saturated solution of zinc sulphate.

Voltaic couple: Zinc^{Hg}—M (metal) (1).

	Pure Metal.	Amalgamated Metal.	Solid Amalgam with Excess of Mercury.	Mercury containing Traces of Metal.
	volts.	volts.	volts.	volts.
Sodium	1.560	.....	1.100	.....
Sodium.....................	1.590	.....	1.460	.....
Potassium	1.680	.....	1.060	.....
Potassium	1.760	.....	1.640	.....
Zinc.......................	0.000	0.000	0.000	0.029 to 0.253
Cadmium	0.311	0.326	0.313	0.540
Tin........................	0.509	0.515	0.510	0.531
Lead.......................	0.509	0.510	0.465	0.494
Iron (2)........	0.497	0.486	0.407	1.258
Copper.....................	1.030	1.014	1.042	.....
Silver (3)..................	1.169	1.275	1.275	.....
Platinum (4)................	1.323	1.169	.....	.....
Brass (5)....................	0.888	0.592	.....	.....
Cannon bronze..............	0.597	0.637	.....	.....
Copper and lead (6).........	0.487	0.512	.....	.....
Copper and lead (7).........	.....	0.509	.....	.....
Silver and zinc (8)..........	.....	0.040	.....	.....
Gold and silver (9)..........	1.030	1.084	.....	.....
Gold and silver (10)	1.208	1.087	.....	.....
Gold and silver (11)..	1.107	1.085	.....	.....
Iron and tin	0.498	0.496	.....	.....
Lead and tin................	0.484	0.409	.....	.....
Lead and zinc...............	0.018	0.018	.....	.....
Silver and copper (12)	0.898	0.996	.....	.....
Silver, zinc, and mercury	0.004	.....	.....	.....
Copper and cadmium........	.....	0.672	.....	.....
Electrolytic bronze..........	0.916	0.064	.....	.....
Mercury....................	1.333	.....	.....	.....

NOTES ON THE PRECEDING TABLES.

(1) In the case of sodium and potassium, the zinc is electro-positive.

(2) Amalgamated by means of sodium amalgam.

(3) Amalgamated by immersion of the hot metal in mercury. The solid amalgam is Diana's tree. Obtained by the action of silver on a solution of mercurous nitrate.

(4) Amalgamated by immersion of a sheet of red-hot plati-

num in boiling mercury.   The solid amalgam has been obtained either by the action of sodium amalgam on platinum chloride, or by heating platinum black with mercury in a sealed tube.

(5) Obtained by electrolysis of a boiling solution consisting of copper sulphate 1 part, zinc sulphate 8 parts, potassium cyanide 18 parts, and water 250 parts.   The anode was a piece of brass prepared from very pure metals, and the cathode a platinum plate.

(6) Amalgam mixed with a great excess of lead.

(7) Amalgam mixed with a great excess of copper.

(8) Silver 1 part and zinc 1 part.

(9) Gold 1 part and silver 3 parts.

(10) Gold 1 part and silver 4 parts.

(11) Gold 1 part and silver 5 parts.

(12) Silver 1 part and copper 1 part.

E. M. F. OF THE COUPLE Zn AND $(Cd + xHg)$. (C. HOCKIN AND H. A. TAYLOR, 1879.)

*Exciting liquid : solution of pure sulphate of zinc.**

Cadmium-mercury (pure)............ 1.232 volts.

Zinc-cadmium 1 p., mercury				5,700,000 p	1.146	volts.
"	"	"	"	3,160,000	1.090	"
"	"	"	"	1,912,000	0.626	"
"	"	"	"	1,450,000	0.572	"
"	"	"	"	1,167,000	0.512	"
"	"	"	"	977,000	0.475	"
"	"	"	"	842,000	0.464?	"
"	"	"	"	742,000	0.475	"
"	"	"	"	662,000	0.472	"
"	"	"	"	598,000	0.462	"
"	"	"	"	407,000	0.456	"
"	"	"	"	314,000	0.451	"
"	"	"	"	153,000	0.438	"
"	"	"	"	101,400	0.428	"
"	"	"	"	76,200	0.421	"

* Neutralized previously by zinc hydrate.

Zinc-cadmium 1 p., mercury	61,100	....	0.420 volts.
" " " "	51,100	....	0.420 "
" " " "	24,240	....	0.410 "
" " " "	6,280	....	0.396 "
" " " "	3,580	....	0.389 "
" " " "	2,515	....	0.386 "
" " " "	1,942	....	0.387 "
" " " "	1,538	....	0.378 "
" " " "	1,339	....	0.376 "
" " " "	1,158	....	0.380 "
" " " "	963	....	0.378 "
" " " "	873	....	0.374 "
" " " "	836	....	0.374 "
" " " "	332	....	0.366 "
" " " "	148.7	....	0.334 "
Zinc-cadmium amalgamated...		....	0.326 "
" " non-amalgamated		....	0.311 "

E. M. F. OF THE COUPLE Zn AND $(Zn + x Hg)$. (C. HOCKIN AND H. A. TAYLOR, 1879.)

Exciting liquid : solution of pure sulphate of zinc.[*]

	Zinc-mercury (pure)........	1.186 volts.
Zinc-zinc 1 p., mercury	23,600,000 p............	1.179 volts.
" " " "	11,800,000	....	1.080 "
" " " "	7,530,000	....	0.655 "
" " " "	5,000,000	....	0.513 "
" " " "	4,720,000	....	0.399 "
" " " "	3,930,000	....	0.257 "
" " " "	3,370,000	....	0.228 "
" " " "	2,700,000	....	0.214 "
" " " "	2,620,000	....	0.214 "
" " " "	1,800,000	....	0.214 "
" " " "	400,000	....	0.134 "
" " " "	200,000	....	0.124 "

[*] Previously neutralized by zinc hydrate.

CHAPTER VII.

CELLS HAVING TWO LIQUIDS.

THE subject is considered under the following classification :

    I. Cells having different electrodes, divided into :
        (1) Cells having liquid depolarizers.
        (2) Cells having solid depolarizers.
        (3) Cells in which depolarization is effected by the development or application of elementary bodies.
    II. Cells having identical electrodes, divided into :
        (1) Cells having liquid depolarizers.
        (2) Cells having solid depolarizers.
    III. Practical data and tables.

I. CELLS HAVING DIFFERENT ELECTRODES.

(1) LIQUID DEPOLARIZERS.

(a) Nitric Acid.
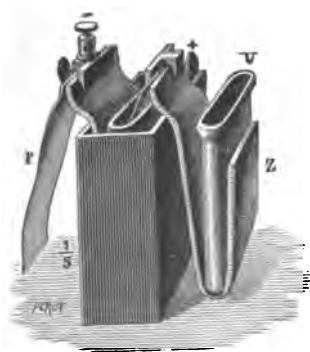
FIG. 59.—GROVE CELL.

Grove Cell (1838).—Zinc^{Hg}, dilute sulphuric acid ; porous cup, nitric acid (D. = 1.33), platinum. E. M. F. = 1.9 volts. The most common form of Grove cell is represented in Fig. 59. The zinc electrode Z is U-shaped and is placed in a porous jar V containing a very thin piece of platinum r. The platinum is connected with the projecting portion of the zinc in the adjoining cell. Poggendorff's arrangement of Grove cell is represented

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in Figs. 60 and 61. The porous jar is cylindrical and con-tains the platinum in the shape of an *S*. The platinum is

FIG. 60.—GROVE CELL.

FIG. 61.—GROVE ELECTRODE.

fastened to a porcelain stopper which almost completely closes the porous jar.

Influence of Temperature on the E. M. F. of the Grove Cell.
(*E. Becquerel.*)

	Temp.	E. M. F.
Grove cell, ordinary zinc......	14° C.	1.598 volts.
" " zinc^{Hg}...........	14° "	1.661 "
" " ordinary zinc	90° "	1.666 "
" " zinc^{Hg}...........	90° "	1.734 "

Royer has substituted oxalic acid for nitric acid in the Grove cell, and has noted its reduction in formic acid. This

reduction is accompanied by a disengagement of hydrogen, but without production of carbonic acid. A saturated solution of furric chloride with 4 per cent nitric acid has been recommended as a substitute for nitric acid.

The chemical reactions (see page 159) produce nitric oxide, which, taking oxygen from the air on escaping, becomes red nitrogen peroxide (NO_4), which gives corrosive fumes. The acid also boils and spatters, so that it is always desirable to use this cell in open air or where there is ample ventilation.

Hawkins (1840) and Olfers (1841) have successively replaced the platinum of the Grove element by a cylinder of passive iron. Iron is rendered passive by plunging it for a few minutes into fuming nitric acid.

Comparative Table of the E. M. F. and Resistance of the Grove Couple in which the Platinum is replaced by Steel, Cast-iron, and Wrought-iron.

Grove cell = 100.

	Resistance.	E. M. F.
Platinum	100.00	100.00
Cast-iron	98.39	89.62
Steel	98.54	86.99
Wrought-iron	85.97	76.88

It is necessary to observe that when wrought-iron, cast-iron, or steel is employed, nitric acid at its maximum of concentration must be used. Wrought-iron by its contact with concentrated nitric acid becomes passive, or, in other words, inattackable by that acid. Cast-iron is not attacked at all by nitric acid and becomes white. On closing the circuit without internal resistance the cast-iron is immediately attacked. This effect ceases as soon as the circuit is open. On the other hand, cast-iron remains passive whenever any external resistance is interposed.

Uelsmann Cell.—$Zinc^{Hg}$, acidulated water; porous cup, nitric acid, silicious iron. Silicious iron is intended to resist attack by dilute nitric acid.

Comparative Table of the E. M. F's of the Callan and Uelsmann Cells, according to the Degree of Concentration of the Nitric Acid.

Nitric Acid.		E. M. F.		Difference.
Quantity, per cent.	Specific Weight.	Silicious Iron. (Uelsmann.)	Cast Iron. (Callan.)	
56	1.460	1.700	1.703	—0.003
50	1.425	1.688	1.693	—0.005
40	1.365	1.670	1.673	—0.003
30	1.270	1.648	1.638	+0.010
20	1.185	1.566	Active*	....
17.5	1.160	<1.	....	....
15	1.135	0.784	....	....
15	1.135	>1.	....	....
15	1.135	1.545	....	....
12.5	1.100	1.470	....	....
10	1.085	<1.	....	....
10	1.085	0.540	....	....
5	1.040	0.514	....	....

* That is to say, the cast-iron ceases to be passive and begins to react on the nitric acid.

Buff Cell (1857).—Zinc, diluted water; porous cup, nitric acid, aluminium. E. M. F. = 1.44 volts.

If the zinc be replaced by tin, iron, copper, or silver, the current retains its direction but loses in E. M. F.

Grove (1839) attempted to substitute wood-charcoal or even retort-carbon for platinum in order to obtain a less expensive cell; but thinking, he says, that in the scientific world only platinum electrodes would be considered as truly " in harmony with science," he makes no reference to carbon electrodes in his memoirs. The substitution was made later by Bunsen.

THE BUNSEN CELL AND DERIVATIVES.

Bunsen Cell (1842) (Fig. 62).—Zinc^{Hg}, dilute sulphuric acid, porous cup; fuming nitric acid, carbon. E. M. F. = 1.96 volts. The zinc is placed in the porous cup, and the carbon in the exterior vessel. By using nitric acid of a density of 1.38,

the E. M. F. of this element becomes equal to 1.89 volts. Archereau reversed the disposition of the electrodes of the Bunsen cell, and placed the carbon in the porous cup, and the
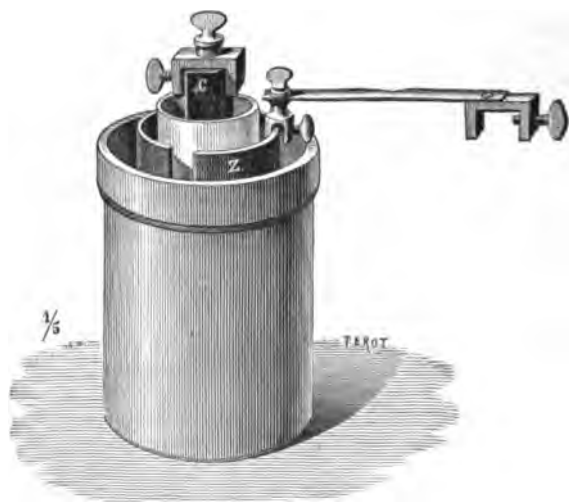
FIG. 62.—BUNSEN CELL.

zinc in the exterior vessel; and this is the arrangement now most commonly employed.

Researches of d'Arsonval on the Electric Constants of the Bunsen Cell.—The cell tested by d'Arsonval had the following features: height, 20 cm.; exciting liquid, sulphuric acid, diluted with $\frac{1}{30}$ of its volume; depolarizer, nitric acid of 36° to 40° Baumé; internal resistance, 0.08 to 0.11 ohm; E. M. F., 1.8 volts. With the acid at 30° the cell weakened rapidly. When nitric acid marks 36° to 32° Baumé, the Bunsen couple consumes 1.30 grams of zinc per ampere-hour; Faraday's law indicates 1.295 grams.

Researches of E. Meylan (1886) *on the Electric Constants of the Bunsen Cell.*—Exciting liquid, 1.5 litres of acid to 11°.5 Baumé (3 volumes of sulphuric acid at 60° Baumé + 3 volumes of water); depolarizer, 0.425 litre of nitric acid at 36° Baumé; active surface of amalgamated zinc, 7.5 square decimetres;

externalfiresistance, 1.27 ohms; internal resistance, 0.04 ohm after setting up, minimum 0.035—it returns finally to 0.12.

E. M. F.

After setting up....... .... 1.93 volts.
 "   15 minutes, closed circuit........... 1.87 "
 "   24 hours, closed circuit............. 1.77 "
 "   30   "   "   "   .... 1.73 "

Variation of Current.

After 15 minutes, closed circuit........ 1.42 amperes.
 "   24 hours, closed circuit.......... 1.33   "
 "   30   "   "   "   .... 1.24   "

Work Done.

After 24 hours of closing............ 56 watt-hours.
 "   30   "   "   "   70   "

Work done with a variation of 10 % *in current-yield of* 1.5 *amperes.*

Time in hours........................... $28\frac{1}{4}$
Watt-hours............................... 65
Weight in kilograms....................... 4.20
Kilogrammetre per kilogram................ 5.60
Average yield............................ 0.96
Useful work per kilogram................. 5.40

Actual Quantity of Nitric Acid utilized in the Bunsen Cell. —D'Arsonval, experimenting under protection from air, has observed that the product of the deoxidation of nitric acid is formed by pure hyponitric acid (NO_2).

The hydrogen, due to the decomposition of the acidulated water by the zinc, reduces nitric acid to the state of nitrogen binoxide (NO); but this compound cannot exist in the presence of concentrated nitric acid by reason of the following reaction:

$$NO + N_2O_5 = 3NO_2.$$

Whence it results that in the Bunsen cell nitric acid yields to the hydrogen but a half molecule of oxygen and becomes transformed into hyponitric acid.

The current remains constant as long as the strength of the nitric acid does not fall below 28° Baumé. Ordinary commercial acid sold for 36° Baumé contains on an average 45% of anhydrous nitric acid.

Consequently the quantity of acid actually utilized in the cell is 45 − 32 = 13 grams per 100 grams of commercial acid or 130 grams per kilogram.

Thermic Reactions of the Grove or Bunsen Cell and of Cells derived from them.—In these couples there is formation of dissolved sulphate of zinc and reduction of nitric acid. The heat of formation of dissolved zinc sulphate is equal to 107 cal., and the heat disengaged by the deoxidation of nitric acid is equal to 13.76 cal. or 27.3 cal. (Favre), according as there is production of nitrogen binoxide and oxygen or nitrous acid and oxygen.

In the first case we have

$$107.0 \text{ cal.} - 13.76 \text{ cal.} = 93.2 \text{ cal.},$$

and in the second case

$$107.0 \text{ cal.} - 27.3 \text{ cal.} = 79.7 \text{ cal.}$$

If these two reactions be regarded as taking place at the same time per equal parts, the quantity of disposable heat should be the mean or 86.47 cal.

These results have been verified by Favre, who has directly found, by the aid of the mercury calorimeter, that the total quantities of heat are substantially those indicated by theory.

And, in fact, if 86.47 cal. be divided by the volt (which corresponds to 46.3 cal.), a value is obtained very closely approximating that found by electric methods ; or

$$\frac{86.47}{46.3} = 1.86 \text{ volts.}$$

No account has been taken of the decomposition of water by the zinc in these couples, for it is compensated for by the recombination of the hydrogen with the oxygen of the nitric acid.

According to Thomsen, the chemical and thermic reactions of the Bunsen or the Grove cell may be represented by the following equations :

(*a*) Chemical reaction :

$$Zn + SO_4H_2 + 2NO_3H = SO_4Zn + 2NO_2 + 2H_2O.$$
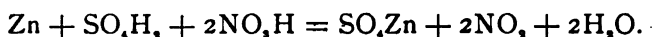
(*b*) Thermic reaction :

$$(Zn,O,SO_4H_2Aq) - (N_2O_4,O,H_2O).$$
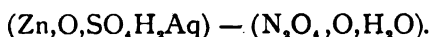
Or,

$$106.090 \text{ cal.} - 10.010 \text{ cal.} = 96.080 \text{ cal.}$$

If, however, 96.080 be divided by the volt, a higher value is obtained than that directly found by electric measurements ; or

$$\frac{96.08}{46.3} = 2.07 \text{ volts.}$$

According to D. Tommasi, in order to calculate the E. M. F. of nitric acid cells of the Grove or Bunsen type by means of thermic data, it is necessary not only to know all the different products which result from the reduction of nitric acid, but also to know in what proportion they are associated.

Now, all that is known at present is that, besides hyponitric and nitric acids, there is formed a small quantity of nitrogen and traces of nitrogen protoxide. On the other hand, Royer and D. Tommasi have found in the porous cup as well as in the external vessel of nitric acid cells a varying quantity of ammonia, determinable by testing with powdered lime and water. The respective proportions of these different products are not yet accurately reported.

Modifications of the Bunsen Cell.—Reinsch (1848) re-placed the carbon with coke in powder, in which was embedded a piece of solid coke serving as electrode.

Liais and Fleury (1852) replaced the porous cup by a carbon containing a cavity filled with nitric acid.

Miergues (1868) used as a negative electrode a carbon bottle closed with a carbon stopper. This bottle was filled with nitric acid and served both as an electrode and as a porous cup.

Faure (1880) also proposed the use of a carbon bottle filled with nitric acid, and, according to Niaudet, this arrangement allows of a more advantageous use of the oxygen of the nitric acid than is possible in the ordinary Bunsen cell.

According to Balsamo, it is advantageous to pour over the surface of the nitric acid, turpentine, which greatly decreases the nitrous emanations and becomes itself transformed into numerous isomeric essences.

Archereau has proposed to cover the cell with an inverted vessel containing a certain quantity of tin, scrap shavings, etc., which will absorb the nitrous vapors.

Also, for the purpose of suppressing the disengagement of nitrous emanations, Ruhmkorff used nitric acid filtered through crystals of potassium bichromate, and Poole Levison (1869) has proposed to add to the nitric acid a mixture of potassium bichromate and sulphuric acid.

Croissant has asserted that the strength of Bunsen cells may be augmented by covering the carbons with a layer of calcined oxide of tungsten.

Boettger (1868) has placed in the porous cup carbon impreg-nated with nitric acid. The carbon is immersed in nitric acid and then is allowed to dry in air twelve hours.

Omeganck has substituted for acidulated water a solution of mercuric sulphate.

Zaliwski-Mikorski (1866) has covered the zincs with the thinnest possible layer of mineral oil, which, according to him, allows of omitting the amalgamation of the zinc and increases the duration of the current.

CELLS DERIVED FROM THE BUNSEN CELL.—*Jedlick and Csapo Cell* (1855).—Zinc^{Hg}, acidulated water; quadrangular porous cup on nitro-cellulose, nitric acid, carbon. The external vessel is made of a mixture cast from iron peroxide, sulphur, and asbestos. The porous cup is formed of paper dipped in concentrated nitric acid, and made to adhere by means of collodion. The use of " nitric paper " as a diaphragm in cells was proposed, in 1854, by Frascara.

The porous cup is placed between two plates of zinc, which causes the cell to resemble that of Wollaston. The upper part of the carbon is dipped first in a bath of stearine and then copper-plated.

Liais and Fleury Cell.—Zinc^{Hg}, sulphuric acid, diluted: porous cup, sulphuric acid. Carbon placed in a circular trough containing nitric acid.

L. Maîche Cell (1864).—Iron, dilute nitric acid; porous cup, concentrated nitric acid, carbon. E. M. F. = 1.5 volts. This cell has the advantage of not disengaging much nitrous vapor, and of being quite constant. The results of chemical reaction are iron nitrate, ammonium nitrate, and probably ammonium nitrite. Theoretically, the only gas which should be disengaged is nitrous oxide, N_2O, but in reality there is always produced a small quantity of nitric oxide due to the composition of nitric acid in the porous cup caused by the action of light and by the effect of the current when the circuit is closed.

Other inventors have attempted to substitute iron for the zinc in the Bunsen cell, using it sometimes in the form of shavings or filings, or sometimes making the external vessel out of it.

Rousse Cell No. 1.—Iron, ordinary water ; porous cup, nitric acid, carbon. E. M. F. = 1.2 volts. A layer of 2 or 3 cm. of oleic acid flows on the nitric acid and serves to prevent nitrous vapors. It becomes transformed into elaidic acid.

Rousse Cell No. 2.—Lead, ordinary water; porous cup, nitric acid covered with oleic acid. E. M. F. = 1.3 volts. In order to increase the lifetime of these cells, Rousse adds to the nitric acid, which should not be too much concentrated, a small quantity of lead peroxide.

Rousse Cell No. 3.—Ferro-manganese at 85 per cent, sulphuric acid at $\frac{1}{30}$; porous cup, nitric acid, carbon.   Rousse has also devised a cell in which the nitric acid is replaced by potassium manganate.

Archereau Cell.—Copper, dilute sulphuric acid ; porous cup, nitric acid, carbon.   E. M. F. = about 0.5 volt.

Buff Cell (1857).—Aluminium, acidulated water ; porous cup, nitric acid, carbon.   E. M. F. = 1.377 volts.

Rousse Cell No. 4.—Crookes' alloy (2 molecules of antimony and 3 molecules of zinc), acidulated water ; porous cup, nitric acid, carbon.

Partz Cell.—In this cell, Fig. 63, the gravity principle is
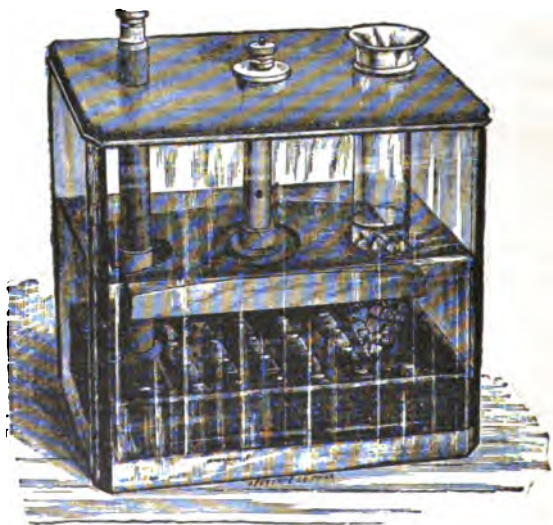
FIG. 63.—PARTZ CELL.

applied to voltaic apparatus of the Bunsen type, in a way similar to that in which it has been applied by Meidinger and others to apparatus of the Daniell type.   The apparatus consists of a glass jar, upon the bottom of which rests the carbon electrode connected by a rod to the upper terminal.   The zinc is suspended from the central rod, and at the right is a glass

tube, funnel-shaped and open at the bottom. In mounting the battery the glass jar is filled just high enough to cover the zinc plate with a solution of either an alkaline sulphate, preferably that of magnesia (1 part in 4 parts of water), or an alkaline chloride, preferably that of ammonium (1 part in 5 parts of water), each cell requiring about 45 fluid ounces. To these solutions may be added from 5 to 10 per cent of hydrochloric acid, which lessens the internal resistance, but causes some local action on the zincs. The depolarization is effected by means of a "sulpho-chromic salt," in which sulphuric acid has been caused to combine with chromic acid in an amorpho-crystalline state. This is dropped into the glass tube, whereupon the carbon cathode soon becomes covered with a dense stratum of depolarizing liquid. When the depolarizer becomes exhausted, a fresh supply of salt is dropped into the tube, thus continuing the action of the battery without interruption.

The E. M. F. of the battery is stated to be 1.95 volts, and its strength of current with different solutions varies from 3 to 7 amperes. A cell tested by Professor Carhart gave initial E. M. F. 2.08 volts: at end of 1 hour closed through 1 ohm external resistance 1.85 volts, but recovered to 2 volts a few minutes after opening the circuit. Internal resistance, 0.82 ohm. Current, 1.04 ampere.

Taylor Cell.—Zinc in form of curved plate, with dilute sulphuric acid in outer vessel ; porous cup, containing depolarizer and eight carbon rods. E. M. F. = 1.9 volts.

(b) Different Acids.

Leblanc Cell (1871).—Zinc, acidulated water ; porous cup, solution of chloric acid, carbon.

The reactions of this cell are as follows :

$$1.\ 3SO_4H_2 + 3Zn = 3SO_4Zn + 3H_2.$$

$$2.\ ClO_3H + 3H_2 = ClH + 3H_2O.$$
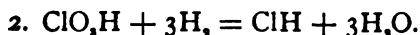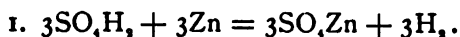
Leblanc has also employed, in place of chloric acid, aqua regia or a mixture of sodium or ammonium nitrate with sulphuric or hydrochloric acid. When the mixture contains hydrochloric acid, the carbon may be replaced by a plate of platinized copper.

In the cell above named, with a mixture of potassium chlorate and sulphuric acid, the total reaction will be represented as follows:

$$ClO_3K + 3SO_4H_2 + 3Zn = 3SO_4Zn + 3H_2O + ClK.$$
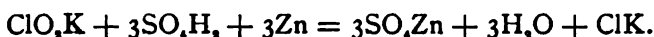
Favre Cell.—Zinc^{Hg}, acidulated water; porous cup, hydrochloric acid, carbon. Chemical reactions are represented by the following:

$$1.\ Zn + SO_4H_2 = SO_4Zn + H_2.$$

$$2.\ ClOH + H_2 = ClH + H_2O.$$
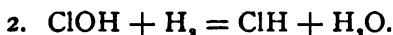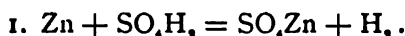
Boettger Cell (1868).—Zinc^{Hg}, solution of sodium chloride and magnesium sulphate, mixed; porous cup, sulphuric acid, antimony.

Kukla Cell.—Zinc^{Hg}, dilute hydrochloric acid; porous cup, concentrated hydrochloric acid, antimony.

(c) Mixed Acids.

Schoenbein Cell (1842).—Zinc, acidulated water; porous cup, mixture of 2 parts of nitric acid and 1 part of sulphuric acid, platinum. The latter acid serves to absorb the water formed by the reduction of the nitric acid by hydrogen.

Leroux Cell (1853).—Zinc^{Hg}, acidulated water; porous cup, mixture of 10 parts of nitric acid and 10 parts of sulphuric acid, carbon.

Zaliwski Cell.—Zinc, saturated solution of sodium chloride containing one fifth part of ammonia; porous diaphragm, mixture of nitric and sulphuric acids, carbon. The elements of this battery are disposed like those of the Cruikshank battery.

Zaliwski-Mikorski Cell (1866).—Zinc, solution of ammonium chloride; porous cup filled with sulphuric acid, in which is placed a second porous cup containing nitric acid and carbon. It is claimed that no effervescence appears and that the zinc is consumed without useless waste.

Wigner Cell (1868).—Zinc^{Hg}, acidulated water; porous cup, depolarizing mixture, carbon. The depolarizing mixture contains nitric acid (D. = 1.360) 200 grams; sulphuric acid (D. = 1.845) 500 grams.

The object of these different mixtures is to utilize the greatest possible quantity of nitric acid, for it is important not to lose sight of the fact that acid which will no longer yield a constant current, and which is consequently rejected, still contains 32 per cent of anhydrous acid. As nitric acid at 36° Baumé contains 45 per cent of anhydrous acid, it therefore does not give up to the hydrogen of the cell but about $\frac{1}{10}$ of the oxygen which it should theoretically yield.

Reinch Cell.—Zinc^{Hg}, acidulated water; porous cup, aqua regia, and crushed coke.

Sosnowski Cell (1866).—Zinc, solution of potash or soda; porous cup, acid mixture, carbon. The acid mixture consists of one volume each of nitric acid at 36° B., sulphuric acid at 26° B., hydrochloric acid, and water. The E. M. F., according to E. Meylan, is 2.376 volts with the potash and 2.370 volts with the soda solution. The reactions occurring are stated by M. Meylan as follows:

"Considering the potash cell as an example, depolarization takes place with formation of nitrogen binoxide according to the symbols

$$3NO_3H + 3H_2SO_4 + 6H = 3H_2SO_4 + 2NO + 4H_2O.$$
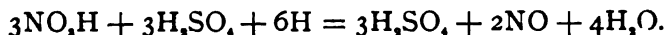
The sulphuric acid is re-formed integrally, and for one atom of hydrogen absorbed we have

$$\tfrac{1}{3}NO_3H + H = \tfrac{1}{3}NO + \tfrac{2}{3}H_2O.$$
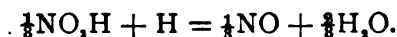
" The heat gained by this reaction is 8.6 calories. The primary action of the current causes decomposition of the potash with formation of zinc oxide and water, and the decomposition of the nitric acid, transformed into potassium nitrate, with liberation of hydrogen. The zinc oxide would then give place to an alkaline zincate, while the hydrogen would act on the depolarizer, as we have seen.

$$Zn \mid 4KOH \mid 2NO_3H = ZnO + H_2O + 2NO_3K + 2H$$
$$= ZnOK_2O + H_2O + H_2O + 2NO_3K + 2H.$$
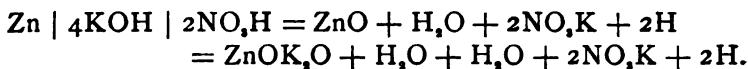
The reaction referred to the hydrogen atom would then be

$$\tfrac{1}{2}Zn + 2KOH + NO_3H = \tfrac{1}{2}ZnOK_2O + NO_3K + H,$$
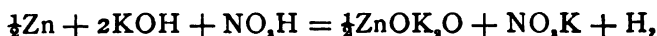
which may be decomposed into two reactions :

$$(a)\ KOH + NO_3H = NO_3K + H_2O,$$
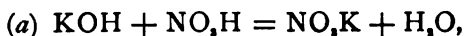
corresponding to 14.4 cal. ; and

$$(b)\ \tfrac{1}{2}Zn + KOH = \tfrac{1}{2}(ZnK_2O) + H,$$
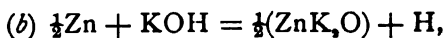
corresponding to 31.6 cal.

" The heat gained in the sum of these reactions is 46 calories. Finally, the chemical heat would be 54.6 calories, which corresponds to an E. M. F. of 2.35 volts. The result of this calculation is not far from that actually determined, the average of the E. M. F.'s at the moment of establishing the potash cells being 2.376 volts.

" For soda the reaction (a) above given yields very nearly the same heat. As the average of the E. M. F.'s of the soda cells has given 2.37 volts, the reaction (b) or the formation of the soda zincate should likewise furnish the same heat. There are, however, no available data on the subject.

" As verification of the heat of formation of the zincate,

which is calculated by a somewhat devious method, the heats of formation C of the zincates of the average alkali zinc-carbon cells have been determined directly by the method of E. M. F.'s. Thus,

(K) $C = 1.3$ volts $\times$ 23.2 $=$ 30.2 cal. ;

(Na) $C = 1.25$ volts $\times$ 23.2 $=$ 29.2 cal.

These values are a little less than those anticipated, but account must be taken of inevitable polarization, unless an electrometer is employed."

D'Arsonval Cell.—Zinc, water acidulated with $\frac{1}{8}$ volume of pure sulphuric acid and $\frac{1}{8}$ of hydrochloric acid ; porous cup, depolarizing mixture, carbon. The depolarizer consists of ordinary nitric acid 1 vol., hydrochloric acid 2 vols., water acidulated $\frac{1}{30}$ by H_2SO_4 2 vols. The carbon consists of a bundle of cylindrical rods of about 1 cm. diameter, separated by intervals of a few millimetres. E. M. F. $= 2.2$ volts. This cell does not polarize on short circuit.

Rouillon Cell (1866).—Zinc, acidulated water, porous cup, aqua regia, silver. The silver on contact with the aqua regia becomes covered with a layer of chloride which prevents further attack. •

Thann Cell (1884).—Zinc[gH], acidulated water ; porous cup containing depolarizing liquid, carbon. E. M. F. $= 1.9$ volts. The depolarizing liquid consists of nitric acid 500 grams, chlorochromic acid 60 grams. The function of the chlorochromic acid is to prevent the formation of nitrous vapors. It has the formula $(C_2O_2Cl_2)$, and is a dark red liquid of density 1.71, boiling at 118° C. It is obtained by the action of concentrated sulphuric acid (30 parts) on a mixture of 10 parts of potassium bichromate and 17 parts of sodium chloride previously pulverized and fused together.

Duchemin Cell (1867).—Zinc, acidulated (or salt) water ; porous cup, solution of picric acid to which sulphuric acid is added, carbon. The porous cup can be omitted here, convert-

ing the arrangement into a single-liquid cell. The hydrogen from the decomposition of the water reduces the picric acid to the state of picramic acid according to the equation

$$(C_6H_2(NO_2)_3OH) + 3H_2 = C_6H_2(NO_2)_2NH_2,OH + 2H_2O.$$

Renard Chlorochromic Battery is represented in Fig. 64. The battery generally has the form of a cylinder of a length ten
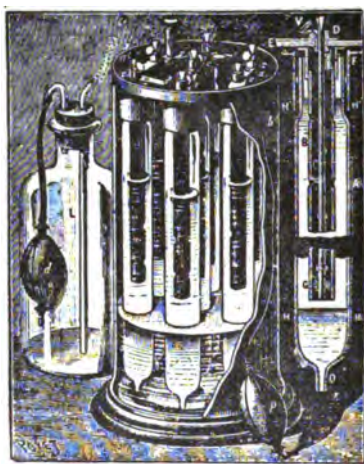
FIG. 64.—RENARD CHLOROCHROMIC BATTERY.

times its diameter. In the pneumatic battery designed for lighting, the elementary vessels, *A*, are sealed to the cover of a large tight vessel, *H*, and the lower part contains an orifice, *O*, of small diameter. Upon forcing air into the large vessel by means of a rubber bulb, *d*, or of a pump, the liquid is made to rise in all the vessels at once. A cock permits of regulating the immersion of the electrodes and, consequently, the internal resistance of the current. This arrangement is adapted to attenuated liquids only; with the normal liquid the cooling would not proceed quickly enough. The vessel, *L*, and the bulb, *d*, serve to fill and empty the battery. The negative elec-

trode of the light batteries is formed of a tube of platinized silver 0.1 mm. in thickness. The weight of the platinum on the two surfaces is about one-tenth that of the silver, and its thickness is about $\frac{1}{400}$ mm. The use of platinized silver greatly reduces the weight, the volume, and the internal resistance of the elements. On account of the high price of these electrodes, carbon, *B*, is substituted for them in the batteries in which attenuated liquids are employed and in which lightness does not play an essential rôle. In order to facilitate the free circulation of the liquid, and to exhaust all the supply contained in the cylindrical vessel, the tube is split throughout its entire length to a width of a few millimetres. The positive electrode consists of a cylinder of zinc or non-amalgamated zinc wire, whose diameter is about $\frac{18}{1000}$ of that of the vessel, and it is calculated to serve but once. This is guided and held in the centre of the platinized silver tube by several disks of ebonite. The solution employed consists of free chromic acid and hydrochloric acid more or less diluted or mixed with sulphuric acid.

(d) Acids and Salts Mixed.

Dering Cell.—Zinc, solution of sodium chloride; porous cup containing the depolarizer, carbon. The depolarizer consists of sulphuric acid 1 litre, sodium nitrate 200 grams, water 3000 grams.

Holmes and Burke Cell.—Zinc^{Hg}, acidulated water; porous cup, solution of sodium nitrate dissolved in concentrated sulphuric acid, carbon. E. M. F. = 1.92 volts. The nitrous vapors from the porous cup are made to pass through a vessel containing ferrous sulphate, by which they are absorbed.

Callan Cells (1847).—(*a*) Zinc^{Hg}, acidulated water; porous cup, depolarizing mixture, platinized lead. The depolarizer consists of concentrated sulphuric acid 4 parts, nitric acid 2 parts, sat. solution of potassium nitrate 2 parts.

(*b*) Same voltaic combination as the preceding, except that iron is substituted for platinized lead.

Wolcott Gibbs Cell (1878).—Zinc^{Hg}, acidulated water; porous cup, nitric acid (D = 1.4) saturated with ammonium nitrate, carbon.   This solution has an advantage over nitric acid in that it sets free nitrogen and not nitrous vapors.

Salleron and Renoux Cell (1859).—Zinc^{Hg}, acidulated water; porous cup, solution of potassium chlorate to which sulphuric acid is added, carbon.   The carbon has a longitudinal opening and several lateral ones, the former being filled with crystals of potassium chlorate.   E. M. F. is between that of the Bunsen and Daniell elements.

Lacombe Cell.—Zinc^{Hg}, acidulated water; porous cup containing a mixture of saturated solution of potassium chlorate, of ferric sulphate or chloride, and sulphuric acid, carbon. $E = 2.15$ volts.   It is important to be careful in dissolving the potassium chlorate in sulphuric acid—as numerous authors ignorant of chemical reactions somewhat heedlessly advise—inasmuch as serious accidents may result.   The reaction of the acid on the chlorate may even cause violent explosions.   The hydrogen coming from the decomposition of the acidulated water by the zinc first reduces the ferric salt to the state of a ferrous salt, and the latter is peroxidized anew by the chloric acid.   In this cell the permanganate of potassium may be substituted for the chlorate, with the advantage of avoiding chlorine emanations.

Vergnes Cell.—Zinc^{Hg}, acidulated water; porous cup, mixture of potassium bichromate, potassium chlorate, manganesed sulphuric acid (*acide sulfurique manganèsé*), carbon.   Instead of a single porous cup, Vergnes uses two, one inside the other. The small one, which is of porcelain baked harder than the other, is bottomless, and is bottle-shaped above so that it can there be closed by a glass stopper.   This last cup is filled with pieces of crushed and well-calcined coke.   The annular interval between this cup and the first is closely packed with small pieces of granular and very porous coke, so that the two cups are practically united.   A folded plate of platinum passes through both layers of coke and forms a terminal.   The depolarizing liquid consists of a solution of potassium bichromate 16

parts, potassium chlorate 1 part, manganesed sulphuric acid 4 parts.

Delaurier Cell (1870).—Zinc^{Hg}, acidulated water; porous cup, depolarizing mixture, carbon. E. M. F. = 2.16 volts. The depolarizing liquid consists of water 60 parts, chromic acid 25, ferric sulphate 25, English sulphuric acid 30. On account of the high cost of chromic acid the liquid may be indirectly prepared as follows: water 30 parts, potassium bichromate 5, ferric sulphate 4, sodium sulphate 5, and sulphuric acid 25. M. Delaurier has also employed the following depolarizing mixtures:

(1) Water 36 parts, ferrous sulphate 20, monohydrated sulphuric acid 7, and monohydrated nitric acid 1. In order to prepare this liquid the ferrous sulphate is dissolved (under protection from the atmosphere) in the quantity of water indicated. There is then added slowly the sulphuric acid, and after agitation the nitric acid is poured drop by drop into the mixture. "This liquid," says M. Delaurier, "is very energetic and very economical, and it has the great advantage of attacking iron, zinc, and other metals without disengagement of hydrogen or nitrous vapors."

(2) Water 10 parts, lead acetate 29, sodium chloride (which may be replaced by either calcium chloride or potassium acetate) 7.

Koosen Cell (1873).—Zinc^{Hg}, acidulated water; porous cup, depolarizing mixture (*a*) or (*b*), carbon. Mixture (*a*) consists of potassium permanganate (con. sol.) 300 grams, sulphuric acid 100; mixture (*b*), of potassium permanganate 100 grams, sulphuric acid, 250, and water enough to dissolve $Mn_2O_8K_2$. The sulphuric acid should be added in small quantities at a time, and care should be taken to prevent heating. E. M. F. = 2 volts on open and 1.7 volts on closed circuit. In the porous cup are formed potassium sulphate and permanganic acid,

$$2MnO_4K + H_2SO_4 = 2MnO_4H + K_2SO_4.$$
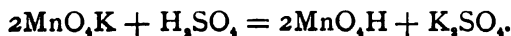
The hydrogen resulting from the action of the acidulated water on the zinc reduces the permanganic acid to the state of protoxide and deprives it of its oxygen in order to form water. The final reaction therefore is

$$2MnO_4H + 7H_2SO_4 + 5Zn = 5ZnSO_4 + 2MnSO_4 + 8H_2O.$$
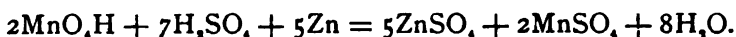
If in this couple platinum be substituted for carbon, the E. M. F. is strongly diminished. The Smee cell, the chromic acid cell, etc., exhibit the same anomaly, as appears from the researches of D. Tommasi on the influence of the negative electrode of the cell on its E. M. F.

D'Arsonval Cell (1881).—Zinc^{Hg}, acidulated water; porous cup, depolarizing mixture, carbon. E. M. F. = 1.8 volts. The depolarizer consists of nitric acid 1 vol., sulphuric acid 1, water 4. This solution is saturated with sulphate of copper in crystals. In this cell the nitric acid is reduced by the copper coming from the reduction of the sulphate instead of by hydrogen. "The copper," says M. d'Arsonval, "being much more rapidly absorbed [*sic*] by nitric acid than by hydrogen, the intensity of the current which this element can yield is greatly augmented."

A. Dupre Cell (1885).—Zinc^{Hg}, water to which sodium chloride or potassium bisulphate is added; porous cup, depolarizing mixture, carbon. E. M. F. = 1.5 to 1.7 volts. The depolarizer contains water 600 grams, sodium nitrate 510, potassium bichromate 60, and sulphuric acid 720. In this cell the nitrous vapors, instead of being disengaged, are absorbed by the bichromate. Ruhmkorff proposed the use of the salt for this purpose in 1867.

Chapman-Anderson Cell.—Zinc, solution of ammonium chloride; porous cup, dilute hydrochloric acid, carbon. In the porous cup there is a perforated tube containing a mixture of potassium bichromate and double oxalate of chromium and potassium. It is not stated whether this is the *blue* oxalate, $(C_2O_4)_6Cr_2K_6, 6H_2O$, or the red oxalate, $(C_2O_4)_2CrK_3, 8H_2O$. Blue oxalate is obtained by saturating potassium bioxalate

(C_2O_4HK) with chromic hydrate ($Cr_2O_3, 6H_2O$ or $Cr_2O_3, 5H_2O$ according to its mode of preparation); while red oxalate is prepared by saturating potassium quadoxalate with chromic hydrate ($C_2O_4HK, C_2H_2O_4, 2H_2O$).

Mauri Cell (1881).—Zinc^{Hg}, salt water or dilute hydrochloric acid; porous cup, depolarizer, carbon. The depolarizer contains potassium chlorate 50 grams, potassium nitrate 25, mercuric chloride 4, and iodine 5. The mixture is moistened with pure water and the diluted hydrochloric acid is added drop by drop. The acid reacting on the mixture produces chlorine and chloride of iodine, which act as depolarizers.

Kukla Cell.—Zinc^{Hg}, salt water; porous cup, nitric acid to which a small quantity of binoxide of manganese is added, antimony.

Buff Cell.—Zinc, salt water; porous cup, concentrated solution of ferric chloride to which hydrochloric acid is added, carbon. E. M. F. between those of the Bunsen and Daniell cells.

Gerardin Cell (1866).—Iron plate surrounded with iron turnings; porous cup, solution of ferric chloride with aqua regia, carbon.

Delaurier Cell (1870).—Iron, salt water; porous cup, depolarizer, carbon. The depolarizer contains water 40 parts, ferric sulphate 25, sulphuric acid 6.

Balsamo Cell.—Lead, 8% sol. of oxalic acid; porous cup, nitric acid to which potassium nitrate is added, carbon. The surface of the liquid is covered with turpentine, which is claimed to increase the constancy and the duration. When the cell has operated for some time, a white precipitate appears of hydrate, oxalate, and carbonate of lead.

(e) Bichromate Cells.

Poggendorff Cell (1842).—Zinc^{Hg}, water to which sulphuric acid or sodium chloride is added, solution of bichromate (1) or (2), carbon. E. M. F. = 2 to 2.2 volts. Formula (1):

water 1000 grams, potassium bichromate 100, and sulphuric acid 50. Formula (2): water 1000 grams, potassium bichromate 166, and sulphuric acid 222. Tissandier's formula: water 1000 grams, potassium bichromate 160, sulphuric acid at 66°, 570. Very ingenious arrangements of this cell have been devised by Radiguet, Jarriant, Baudet, Fuller, Higgins, and others.

Jarriant-Goldner Cell.—This is constructed, as shown in Fig. 65, with an external vessel of wood lined with lead. The
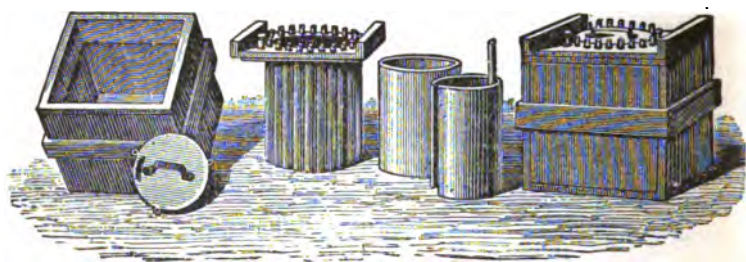
FIG. 65.—JARRIANT-GOLDNER CELL.

·depolarizing liquid is at the outside of the porous cup, and the negative electrode consists of 16 circularly-arranged carbon pencils, the conical heads of which are received in holes formed in the cover. The hollow zinc cylinder which forms the positive electrode is placed in a circular groove made in the bottom of the porous cup, this groove containing a sufficient supply of mercury to amalgamate the zinc. The depolarizing solution contains sodium bichromate 5 parts, water 8, and sulphuric acid at 66° 10. The E. M. F. is 2.2 volts on open and 1.9 volts on closed circuit.

Radiguet Windlass Battery.—In this device (Fig. 66) the zincs are fixed upon a wooden frame which is supported by a cord or chain from the windlass shaft. By suitably rotating the latter the zincs may be raised out of or lowered into the exciting liquid contained in the several vessels. Another arrangement by Radiguet is shown in Figs. 67 and 68. Each cell here consists of a vessel of earthenware, a carbon cylinder, an amal-
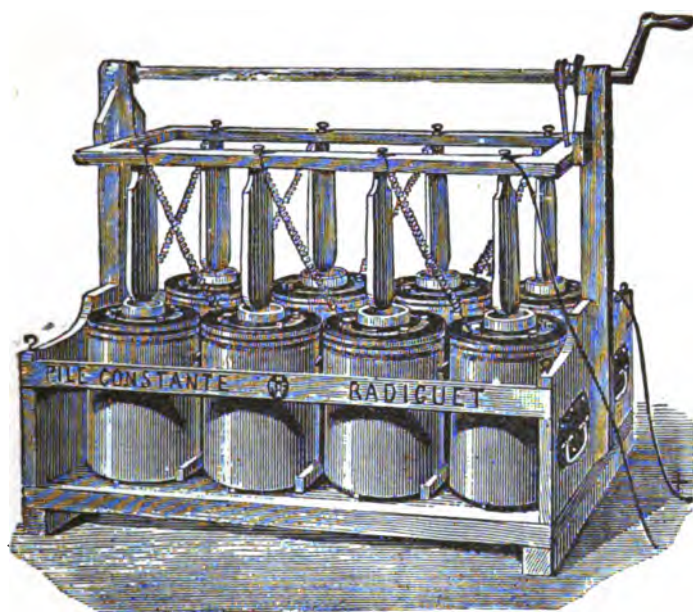
FIG. 66.—RADIGUET BATTERY.
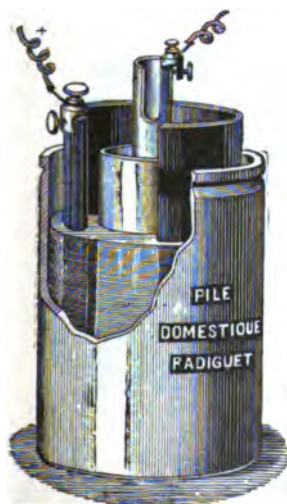
FIG. 67.—RADIGUET CELL.

FIG. 68.—RADIGUET CELL.

gamating support and its cup, these parts being assembled as shown. The amalgamating support consists, as represented in Fig. 68, of a tube carrying a sort of basket or tray, which re-
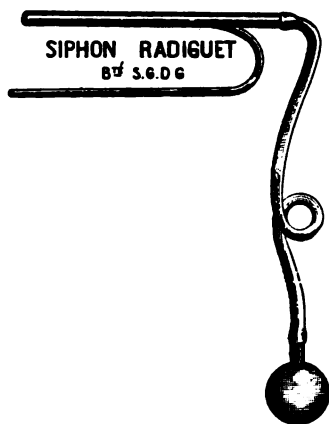
SIPHON RADIGUET
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ceives the zinc in the shape of shavings or balls. Under the tray and connected to it by two conducting rods is a cup or trough containing zinc amalgam. The composition of the depolarizer is the same as used in the swinging cells described in the following paragraph. In order to remove spent liquid from the cell M. Radiguet has devised the siphon represented in Fig. 69, which it will be noted is set in operation by forcing in air by means of a rubber bulb and tube.

FIG. 69.—RADIGUET SIPHON.

Radiguet Swinging Cells.—In this device (Fig. 70), by a single movement of a lever the zincs are removed from the
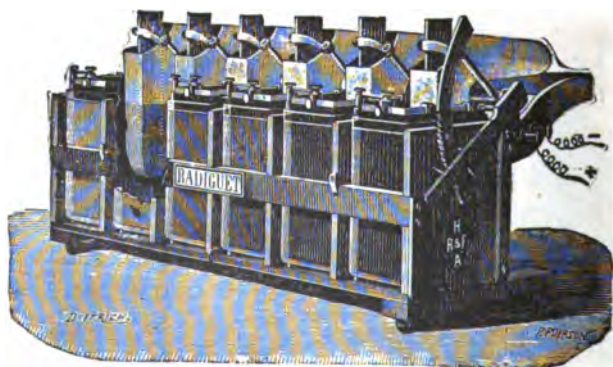
FIG. 70.—RADIGUET BATTERY.

acidulated water and the two liquids are separated. Figs. 71 and 72 are vertical sections of a cell of this type. The ex-

ternal vessel, *D*, contains the carbons and the bichromate solution. The tilting vessel, *E*, is heart-shaped and really consists of two distinct vessels, *F* and *F'*, disposed relatively at right angles. The vessel *F* is of porous earthenware, and enters the bichromate solution when the cell is in operation, as shown in Fig. 71. The compartment *F'* is of enamelled porcelain. When the cell is out of operation the water in the
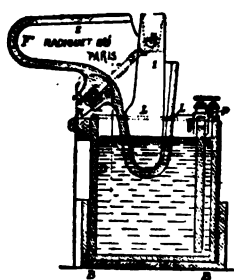
FIG. 71.   RADIGUET SWINGING CELL.   FIG. 72.
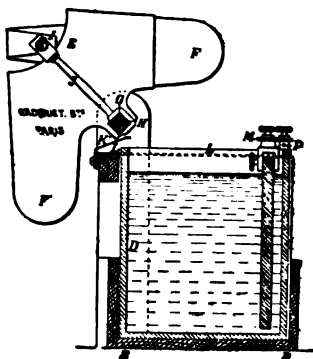
porous compartment *F* is turned into the non-porous or enamelled portion *F'* and the part *F* is raised out of the bichromate. The zinc supported by the column *I* follows the rotary movement of the vessel *E* and is thus removed from the liquid. The arrangement is such that all the cells of a battery can be moved and the immersion of the porous cups regulated by the operator with one hand. In order to charge a battery of six cells Radiguet uses the following solutions:

Exterior vessel:

Water....................... 3400 grams.
Sodium bichromate............ 800   "
Sulphuric acid................ 1000   "

Porous vessel:

Water....................... 400 grams.
Sulphuric acid................ 72   "

C. Baudet Cells (1881).—Carbon, solution of potassium bichromate, porous cup, dilute sulphuric acid zinc[Hg]. E. M. F.

= 2 volts. In Fig. 73, *A* is the outer-containing vessel, *B* the porous cup containing the zinc, *F* a receptacle for bichromate of potassium crystals, *G* receptacle for sulphuric acid, *D* zinc, and *C* carbon. The two receptacles, *F* and *G*, are both porous, and receptacle *F* is perforated. In the unperforated vessel, *G*, is placed sulphuric acid.

FIG. 73.—BAUDET CELL.

A siphon battery by M. Baudet consists of a frame containing 12 cells placed one beside the other as shown in Fig. 74. On an upper shelf of the frame are two glass tanks containing exciting liquid. The
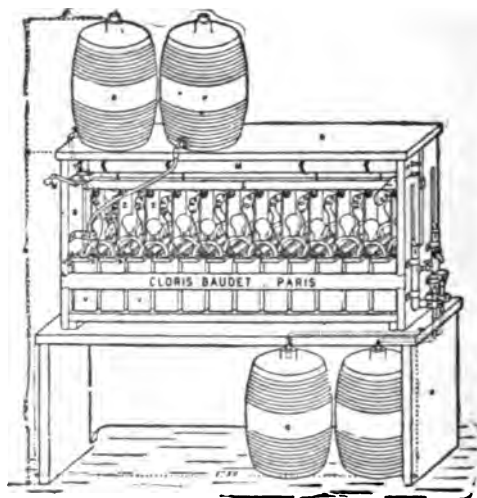
FIG. 74.—BAUDET SIPHON BATTERY.

frame is placed on a bench beneath which are arranged two other receptacles for the spent liquid. Each cell is

composed of a rectangular outer vessel of glass in which is placed a porous cup containing a plate of zinc^{Hg}. On each side of the porous cup are two plates of carbon. The cells communicate with one another by means of siphons (Fig. 75) which extend between adjacent cells, the arms entering the external vessels, the longer arm of each siphon being turned from the side whence the liquid comes. A similar disposition establishes communication between the porous cups. The siphon is started by pressing the rubber bulb, S, which is
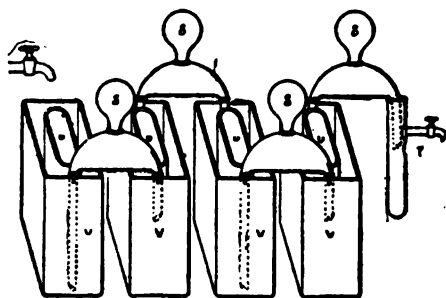
FIG. 75.—BAUDET SIPHONS.

arranged on the upper portion of each siphon so as to drive the air from and draw the liquid into it. The zincs are carried by a windlass, so that they may be raised or lowered into and out of the cells. The valves communicating with the supply vessels with those intended to receive the spent liquid and also the escape valves are opened. The fluids used in this cell are as follows: Depolarizer—water 1000 grams, potassium bichromate in powder 100, sulphuric acid at 66° 180; exciting liquid —water 1000, sulphuric acid at 66° 50.

Camacho Battery (Fig. 76).—The cells are arranged in battery in cascade, that is to say, they are placed on different horizontal planes. The bichromate solution flows continuously from a reservoir into the first porous cup, whence it circulates

through the following cups, and finally is collected in a receiving vessel.
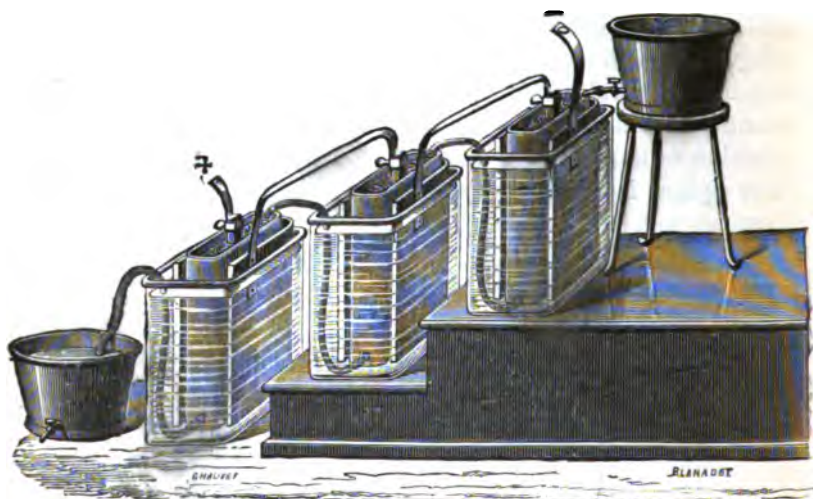
FIG. 76.—CAMACHO BATTERY.

Crowdus Cell (Fig. 77 and 78).—The construction is such that the connections are made through the bottom of the cell to terminals on the exterior at one side or at the ends. The containing vessel has a removable bottom, a, and a false bottom, b, leaving the space c between them for the wire connections. Above the false bottom is a porous partition, B, dividing the cell into the two chambers d and e, in the former of which is the electrolyte for the negative plate, and in the latter that for the positive. The negative electrode, C, consists of a plate of porous carbon placed close to the partition, so as to assist the latter in preventing the mixing of the electrolytes, while the positive electrode, E, stands with its lower edge in a mercury bath, D. The sides of both plates rest in grooves in the walls of the cell. The mercury trough is formed of metal and placed at the lowest point of the chamber, as shown at g. The connecting wire h is soldered to the trough and drawn down

through the false bottom. The wire *i* similarly connects with the bottom of the negative plate by passing through the bottom *b*. If the plate be of carbon, its lower edge is electroplated with copper. A bar of metal is then soldered to one
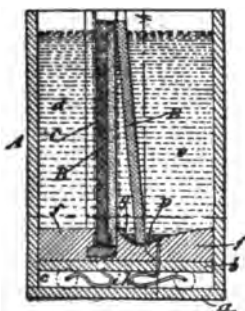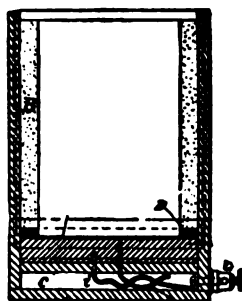
FIG. 77.   CROWDUS CELL.   FIG. 78.

side of this copper rim and the wire *i* embedded in or soldered to the bar. The wires *h* and *i* are carried through the bottom space to either side of the cell, and pass out through holes for connection with binding posts. The bottom *a* is made removable, so that the connections can be properly arranged before it is fastened on. This is the construction for single cells.

Fuller Cell (1871) (Fig. 79).—The zinc electrode is in the shape of a rod carrying a pyramidal or conical mass which is placed in the porous vessel together with about 30 grams of mercury. The carbon plate is in the outer glass vessel, which is filled with a solution of 90 grams potassium bichromate in 1 part of sulphuric acid and 9 parts of water. Water only is poured into the porous cup. The mercury keeps the zinc well amalgamated. This is an excellent form of cell. Its E. M. F. = 2.14 volts and reaches its maximum in the course of a few hours after setting up, and the current is constant. On an ordinary working circuit no extra bichromate crystals will be required for six months after starting, nor indeed so long as the solution remains of an orange color. The internal re-

sistance, by varying the thickness of the porous vessel and the strength of the solution, may be made to vary from $\frac{1}{2}$ ohm to 4 ohms, according to the work to be done. This cell is more economical than the Daniell. It is largely employed in England for telegraph purposes.

Goarant de Tromelin Cell.— Zinc, solution of ammonium chloride ; porous cup, concentrated solution of potassium bichromate to which sulphuric acid is added, carbon.

Gandini Cell.—Zinc, solution of chloride of sodium or ammonium ; porous cup, dilute solution of potassium bichromate to which sulphuric acid is added, carbon. E. M. F. = 1.4 volts. At a temperature of 15° C. and a resistance of .82 ohm the E. M. F. is 2.10 volts. At a temperature of 100° C. and a resistance of .71 ohm the E. M. F. is 2.44 volts.

FIG. 79.—FULLER CELL.

Nystrom Cell (1881).—Zinc^{Hg}, acidulated water ; porous cup, sulphuric acid to which a little potassium bichromate is added, carbon.

Slater Cell (1881).—Nickel, acidulated or salt water ; porous cup, solution of potassium bichromate, carbon. E. M. F. = 1.5 volts (?).

Thomsen Cell (1860).—Copper, acidulated water containing 1 part of sulphuric acid to 4 parts of water ; porous cup, solution of potassium bichromate to which sulphuric acid is added, carbon. E. M. F. = 0.9 volt. The copper is attacked only on close circuit.

Favre Cell.—Zinc^{Hg}, dilute sulphuric acid ; porous cup, chromic solution, platinum. E. M. F. = 1.35 volts.

The chromic solution contains crystallized chromic acid 25 grams, sulphuric acid at 66° 18, water 50. According to Favre

this couple should disengage 117.3 cal. (2.5 volts), but only 62.5 cal. (1.35 volts) would be transmissible to the circuit.

D. Tommasi (1882), resuming the study of this cell, has observed the following facts: That the chromic acid couple, such as Favre used, that is to say, having its negative electrode of platinum, produces external chemical work equal only to about 65 cal. (1.4 volts). Second, that by substituting for the platinum in this same cell carbon or platinum sponge, it becomes possible to send to the circuit 85 cal. about (1.8 volts), or 20 cal. (0.45 volt) in excess of that of the preceding cell. Similar results could no doubt be obtained by replacing the chromic acid with a mixture of bichromate and sulphuric acid.

Fitz-Gerald and Molloy Cell (1876).—This cell consists of a vessel separated into two compartments by a partition of carbon which forms the negative electrode and which contains a large number of holes filled with porous earth. In one of the compartments the zinc is immersed in dilute sulphuric acid. The other receives a mixture of chromate of lime to which sulphuric acid is added.

Maquay Cell (1886).—The positive electrode is composed of an alloy containing mercury 1 part by weight; tin 2, lead 2, and zinc 95. This electrode is amalgamated exteriorly in the usual way. The negative electrode consists of carbon covered with a thin layer of sulphur, or pieces of sulphur may be placed in the porous cup around the carbon. The zinc alloy is placed in a solution of sulphuric acid or sodium chloride. The carbon is contained in a porous cup with the material of which a certain amount of powdered carbon is mingled, and in which cup there is a depolarizing liquid consisting of potassium bichromate 35 to 40 parts, sulphuric acid 10 to 20 parts, nitric acid 40 to 55 parts.

In order to determine whether the bichromate solution is expended or not, to a small quantity of it placed in a test-tube add a few drops of nitrate of silver. If the solution still contains any chromic acid, there will be a red precipitate of silver chromate.

Kousmine Diffusion Cell.—By making use of the phenome-

non of diffusion, M. Kousmine has succeeded in overcoming the increase in internal resistance of the bichromate of potash battery due to the formation of crystals on the negative electrode. The carbon electrode consists of four strips attached to the lid of the battery. The zinc electrode consists of a circular grating resting on the bottom of the battery. By means of a funnel a 15-deg. Baumé solution of sulphuric acid is introduced until it just reaches the lower end of the carbon strips. A 6 to 7 per cent solution of bichromate of potash is next introduced. The two liquids do not mix on account of the great difference in their densities. When the battery is short-circuited it is easy to see that chemical action only takes place close to the lower end of the carbon strips, which are gradually surrounded by a violet ring two or three millimetres deep. Above this region the bichromate solution retains its original color. The bichromate solution being very weak, the chromic crystals dissolve as soon as they are formed, and the negative electrode is not covered by a deposit as in other batteries. The solution of these crystals, having a greater density than the surrounding liquid, falls to the bottom. The sulphate of zinc also falls to the bottom of the cell, causing more sulphuric acid to rise. A cell having the following dimensions has been tested by a committee of experts: height, 20 cm.; diameter, 15 cm.; surface of zinc, 176 sq. cm.; bichromate solution, 6 per cent; sulphuric acid, 15 deg. Baumé. The committee reported that after having been circuited for $8\frac{1}{4}$ hours on an external resistance of .32 ohm, and then left on an open circuit for $10\frac{1}{4}$ hours, the cell continued to work for $4\frac{1}{4}$ hours, when the circuit was again closed, and that it gave during 13 hours 36 ampere-hours for an expenditure of 48 grams of zinc.

Investigations of E. Meylan (1886) on the Potassium Bichromate Cell.—Exciting liquid, 0.5 litre of sulphuric acid diluted $\frac{1}{10}$. Depolarizer, 1.650 litres of a mixture of 200 grams of potassium bichromate, 425 c. cm. of sulphuric acid, and 1300 c. cm. of water. Zinc, well amalgamated: active surface 6.1 sq. dcm. External resistance, 1.16 ohms. Internal resistance

:at the beginning, 0.231 ohm; minimum, 0.22 ohm; final, 0.3
,ohm.

E. M. F.

After mounting...................... 2.015 volts.
"   15 minutes of closed circuit....... 2.00   "
"   24 hours   "   "   "   .... 1.88   "
"   30   "   "   "   "   .... 1.86   "

	Reduction in Per cent.	Coefficient of Utili-zation of Zinc.
After 24 hours of closed circuit..	6.09	0.59
" 30 " " " " ..	7.07	

Variation of the Current.

After 15 minutes of closed circuit..... 1.43 amperes.
"   24 hours   "   "   "   ..... 1.31   "
"   30   "   "   "   "   ..... 1.28   "

<center>Reduction in hundredths.</center>

After 24 hours of closed circuit....... 8.68 amperes.
"   30   "   "   "   "   ....11.14   "
Electric yield after 30 hours = 0.82 to 0.85.

Work Done (Watt-hours).

After 24 hours of closed circuit.................. 61
"   30   "   "   "   "   75

Work Done with a Variation of 10% of the Current-yield = 1.5 Amperes.

Period in hours...................... 30.5
Watt-hours 77
Weight in kilograms.................. 3.69
Kilogrammetres per kilogram.......... 7.50
Average yield....................... 0.82 to 0.85
Useful work per kilogram.............. 6.10

Advantages of Sodium Bichromate.—It has been determined that sodium bichromate possesses decided advantages over potassium bichromate. It has a larger proportion of available oxygen, so that for equal depolarizing capacities about eleven per cent less of it is required than of the potassium salt. It is soluble without the aid of heat, gives a denser solution, and does not weaken so readily. Such double sulphates of sodium and chromium as are formed do not crystallize out, but remain in solution, thus rendering the cell more easily cleaned.

CHAPTER VIII.

CELLS HAVING TWO LIQUIDS. *(Continued.)*

I. CELLS HAVING DIFFERENT ELECTRODES. *(Continued.)*

(I) LIQUID DEPOLARIZERS. *(Continued.)*

(f) Chlorides.

Daniell Cell.—Zinc, dilute sulphuric acid; porous cup, platinum chloride, platinum. This cell was proposed by Daniell as realizing fully the idea of a perfect cell; but he adds, " it would be too expensive."

L. Matche Cell (1865).—Zinc^{Hg}; dilute hydrochloric acid; porous cup, acid solution of stannic chloride carbon. E. M. F. = 1.5 volts.

Duchemin Cell.—Zinc, salt water (100 grams water, 125 grams sodium chloride) ; porous cup, solution of ferric chloride (water 200 grams, ferric chloride at 30° 150), carbon. E. M. F. = 1.35 volts. Under the influence of chloride of sodium the zinc decomposes the water, and the hydrogen, acting on the solution of ferric chloride, reduces it to the state of ferrous chloride. The latter may transform itself anew into ferric chloride either by the action of chlorine or by the addition of a few drops of aqua regia or even nitric acid.

Ponci Cell.—Iron, solution of ferrous chloride at 35° B.; porous cup, solution of ferric chloride at 35° B., carbon. E. M. F. = 0.99 volt. The iron is oxidized at the expense of the water

and disengages hydrogen. The latter reduces the perchloride to the state of protochloride,

$$H_2 + Fe_2Cl_6 = 2FeCl_2 + 2ClH.$$
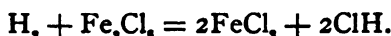
The hydrochloric acid which is produced in this reaction attacks the iron.

$$Fe + 2ClH = Cl_2Fe + H_2;$$
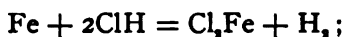
and it is this last reaction which determines the electric current.

D'Arsonval Cell (1881).—Zinc, soda solution; porous cup, ferric chloride, carbon.   E. M. F. = 2.7 volts.

In this cell there is formed ferric hydrate (an insoluble compound) in the pores of the porous cup, which opposes the mixture of the ferric solution with the liquid of the external vessel. D'Arsonval has also devised other cells based on the same principle.

Weare Cell.—Zinc, saturated solution of calcium chloride; porous cup, saturated solution of cupric chloride, copper. The battery is arranged in troughs, and the zinc and copper plates are enveloped in blotting-paper and placed within bags which serve as porous diaphragms. Under the influence of the chloridizing of the zinc, the cupric chloride becomes decomposed. The copper is carried to the negative plate, and the disengaged chlorine replaces the losses in chlorine from the calcium chloride. The residue is zinc chloride.

Roudel Cell.—Zinc, solution of ammonium chloride; porous cup, containing at the bottom mercury, and filled with a solution of double chloride of mercury and potassium to which a certain quantity of the same substance is added in the solid state. The platinum wire is immersed in the mercury and is covered with an insulating coating over all that portion which comes in contact with the double chloride solution.

(g) Hypochlorite.

Niaudet-Breguet Cell (1879).—Zinc, 25% solution of sodium chloride ; porous cup, carbon surrounded with chloride of lime. E. M. F. = 1.6 volts.

In this cell the chloride of lime may be replaced by a solution of hypochlorite of soda (Javelle water), but the E. M. F. of the cell becomes slightly weaker. The hydrogen, due to decomposition of the water, reacts on the chloride of lime to form water and hydrochloric acid, whence there results, in the exciting solution, zinc and calcium chlorides.

(h) Nitrates.

Deroy Cell (1848).—Zinc, sulphate of zinc solution to which sulphuric acid is added ; porous cup, potassium nitrate, platinum.

Rousse Cell.—Lead or iron, water; porous cup, solution of mercurous nitrate, carbon.

D'Arsonval Cell (1881).—(*a*) Zinc, solution of zinc chloride; porous cup, solution of silver nitrate, silver. E. M. F. = 1.15 volts. (*b*) Zinc, solution of zinc sulphate; porous cup, solution of lead nitrate, lead. E. M. F. = 0.6 to 0.75 volt.

In these cells there is formed in the pores of the porous cup a precipitate which in the cell (*a*) is silver chloride, and in the cell (*b*) lead sulphate, both of which are insoluble and which impede the mixture of the solution in the porous cup with that of the external vessel.

D'Arsonval has devised another cell on the same principle, containing as a depolarizer a liquid which gives a precipitate by its mixture with the liquid which attacks the zinc. The diaphragm which separates the two liquids ultimately becomes completely impermeable. The precipitate formed in the porous cup should be both a conductor of electricity and also susceptible to electrolysis.

(i) Sulphates.

Wilbrant Cell.—Zinc, solution of ammonium chloride; porous cup, solution of ferrous sulphate containing crystals of that salt, carbon.

Senet Cell.—Zinc^{Hg}, acidulated water; porous cup, solution of iron alum, carbon.   E. M. F. = 1.7 volts.   The reduction of the iron alum (ammonico-ferric sulphate) furnishes the sulphuric acid necessary for the attack of the zinc.

Van den Eynde Cell.—Zinc, salt water; porous vessel filled with crushed aluminium sulphate immersed in salt water, carbon.

Jacobi Cell.—Silver, solution of potassium cyanide; porous cup, solution of copper sulphate, copper.

(j) Potassium Permanganate.

Rousse Cell.—Ferromanganese at 85 per cent, sulphuric acid $\frac{1}{10}$; porous cup containing a solution of potassium permanganate, carbon.   Sturm assigns to ferromanganese the following composition :

Carbon	6.21
Silicium	0.28
Phosphorus	0.06
Copper	0.14
Manganese	69.64
Iron	23.45

This alloy is made industrially, and especially at the works at Terrenoire, near Saint-Etienne, France.   The salts produced in this cell are sulphate and nitrate of manganese, with sulphate and nitrate of potassium.   Rousse has also devised a cell in which the permanganate is replaced by nitric acid.

Dun Cell (1886).—Zinc, solution of caustic potash (1 part of potash, 5 parts of water); porous cup of carbon, solution of potassium permanganate.   E. M. F. = 1.8 volts.   This cell

works only on closed circuit. After 30 or 40 minutes of short-circuiting the E. M. F. falls to 1 volt; but the cell regenerates and resumes its original electromotive force after one or two hours of rest.

(k) Cells containing a Metal, a Salt containing the same Metal, another Metal, and a Second Salt containing the Second Metal.

Regnauld Cell.—Zinc, solution of sulphate of zinc; porous cup, solution of cadmium sulphate, cadmium. E. M. F. = 0.30 to 0.35 volt.

Chemical reactions are represented by the following:

Principal reaction:

$$Zn + SO_4Cd = SO_4Zn + Cd.$$

Secondary reactions:

(1) $$Zn + 2H_2O = Zn(OH)_2 + H_2.$$

(2) $$H_2 + SO_4Cd = SO_4H_2 + Cd.$$

(3) $$SO_4H_2 + Zn(OH)_2 = SO_4Zn + 2H_2O.$$
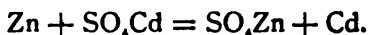
The heat disengaged is 16.6 calories, calculated according to the method of thermic constants.

Callan Cell.—Zinc, solution of zinc sulphate; porous cup, solution of ferrous sulphate, cast-iron.

Dupre Cell (1857).—Zinc, solution of zinc sulphate; porous cup, solution of copper acetate, copper. This cell gives a more energetic current in air than in a vacuum.

Coleman Cell (1885).—Iron, ferrous sulphate; porous cup, solution of copper sulphate, copper. E. M. F. = 0.6 volt.

Regnauld Cell.—Potassium amalgam (1 part potassium to 150 parts of mercury), solution of potassium chloride; porous cup, solution of platinum chloride, platinum. E. M. F. = 2.276 volts.

E. M. F.'S OF CERTAIN CELLS FORMED OF TWO METALS, EACH
IMMERSED IN A SOLUTION OF ITS OWN SALT.

(The saline solutions are separated by porous partition.)

Regnauld's Experiments.

			E. M. F. volt.
Zinc, zinc sulphate	: copper sulphate, copper	....	0.96
" " nitrate	: " nitrate, "	....	0.87
" " chloride	: " chloride, "	....	0.96
" " formate	: " formate, "	....	0.96
" " acetate	: " acetate, "	....	0.96
Zinc^{Hg}, zinc sulphate	: copper sulphate, copper	....	0.69
Zinc, zinc sulphate	: nickel sulphate, nickel	....	0.69
" " chloride	: " chloride, "	....	0.60
" " nitrate	: " nitrate, "	....	0.72
" " chloride	: cobalt chloride, cobalt	....	0.62
" " nitrate	: " nitrate, "	....	0.51
" " sulphate	: cadmium sulphate, cadmium	....	0.30
" " chloride	: " chloride, "	....	0.23
" " bromide	: " bromide, "	....	0.23
" " iodide	: " iodide, "	....	0.25
" " nitrate	: " nitrate, "	....	0.23
Zinc^{Hg}, zinc sulphate :	" sulphate "	....	0.32
" dilute phosphoric acid :	" " "	...	0.32
Cadmium, cadmium sulphate : thallium sulphate, thallium		......	0.043
Zinc, zinc sulphate	: aluminium sulphate, aluminium	..	0.17
" " "	: thallium sulphate, thallium	......	0.34

It follows from this that if the cell be made with two metals,
each entering a solution of one of the salts, and if these salts
be of the same acid, the E. M. F. varies little with the nature
of the acid.

Raoult's Experiments (1863).

			E. M. F. volt.
Zinc, zinc sulphate : cadmium sulphate, cadmium		..	0.345
" " chloride :	" chloride, "	..	0.259
" " bromide :	" bromide, "	..	0.259
" " iodide :	" iodide, "	..	0.270
" " sulphate : copper sulphate, copper		......	1.079
" " chloride :	" chloride, "	......	1.058
" " nitrate :	" nitrate, "	......	0.853

F. Herroun's Experiments (1886).

	E. M. F. volt.
Zinc, zinc sulphate : tin sulphate, tin	0.525
" " chloride : " chloride, "	0.549
" " iodide : " iodide, " (a)	0.485
Cadmium, cadmium sulphate : " sulphate, "	0.189
" " chloride : " chloride, "	0.289
Tin, tin sulphate : copper sulphate, copper	0.560

The solutions used in these cells, except for (a), contain 0.5 per cent chloride or sulphate. The solution used in (a) contains 0.25 per cent iodide and 1 per cent hydroiodic acid.

Experiments of H. Jahn (1886).

	Found at 0°. volt.	Cal- culated.* volt.
Copper, copper sulphate : zinc sulphate, zinc	1.096	1.058
" " " : cadmium sulphate, cadmium	0.678	0.705
Silver, silver nitrate : copper nitrate, copper	0.436	0.416
" " " : lead nitrate, lead	0.914	0.923
Copper, copper nitrate : " " "	0.492	0.507
" " acetate : zinc acetate, zinc	1.104	1.113
" " " : lead acetate, lead	0.496	0.532
Lead, lead acetate : zinc acetate, zinc	0.003	0.579

Experiments of Th. Erhard (1881).

		E. M. F. volt.
$\overset{+}{\text{Zinc, zinc chloride}}$	$\overset{-}{\text{: indium chloride, indium}}$	0.357
$\overset{-}{\text{Indium, indium chloride}}$	$\overset{+}{\text{: ferrous " iron}}$	0.172
" " "	: cupric " copper	0.630
Amalgam of potassium, potassium sulphate : zinc sulphate, zinc		1.000

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* Values obtained by taking the difference of the E. M. F.'s of polarization. Thus:

Zinc, zinc sulphate — copper sulphate, copper = E. M. F.
2.715 volts   —   1.660 volts   = 1.058 volts.

Amalgam of sodium, sodium sulphate : zinc sulphate,
  zinc........ .... 0.96
Magnesium, magnesium sulphate : zinc sulphate, zinc .. 0.79
Zinc, zinc chloride : platinum chloride, platinum....... 1.34

Experiments of A. P. Laurie (1886).

+   —   volt.
Zinc, zinc sulphate : aluminium sulphate, aluminium..... 0.54
  —   +
  "   "   "   :   "   "   "   amalg. 0 46
  +   —
Amalgamated aluminium, aluminium sulphate, aluminium 1.08

  *Effect of the Dilution of the Salts on the E. M. F. of Couples
formed by Two Metals, each entering a Solution of one of its own
salts.*—It appears from Regnauld's researches (1855):

  1. That the concentration of the saline solution in which
the attacked metal of the two-liquid cell is immersed may
vary between very wide limits, from 1 to $\frac{1}{100}$, with modifica-
tion of the E. M. F. of the cell. Thus with the cell (zinc,
zinc sulphate)—(porous cup, cadmium sulphate, cadmium) the
following results are obtained :

Solution of Zinc Sulphate.	Solution of Cadmium Sulphate.	E. M. F.
Saturated at 14°	Saturated at 14°	0.3 volt.
$\frac{1}{2}$ " " "	Constant	"
$\frac{1}{8}$ " " "	"	"
$\frac{1}{10}$ " " "	"	"
$\frac{1}{15}$ " " "	"	"
$\frac{1}{30}$ " " "	"	"
$\frac{1}{40}$ " " "	"	"
$\frac{1}{100}$ " " "	"	"

  The fractions here indicate the ratio of the volume of the
normal solution to the total volume represented by its mixture
with distilled boiled water.
  The foregoing is also true of the following:
  Zinc, zinc chloride : cadmium chloride, cadmium.
  "   "   nitrate :   "   nitrate,   "
  Zinc^{Hg}, dilute sulph. acid : cadmium sulphate, cadmium.
  "   "   "   "   : copper sulphate, copper.

2. That the concentration of the saline solution in which the unattacked metal enters may exert a certain influence on the E. M. F. of the couple. Considering the same cell as before, in which the quantity of water in the cadmium sulphate solution is varied, the zinc sulphate solution being constantly saturated, we have:

Solution of Zinc Sulphate.		Solution of Cadmium Sulphate.			E. M. F.
Saturated at 14°		Saturated at 14°			0.30 volt.
Constant	$\frac{1}{8}$	"	"	"	0.30 "
"	$\frac{1}{10}$	"	"	"	0.30 "
"	$\frac{1}{50}$	"	"	"	0.27 "
"	$\frac{1}{100}$	"	"	"	0.23 "

Regnauld has also found that in the Daniell couple, the zinc sulphate solution remaining constant, the concentration of the copper sulphate solution may vary from $\frac{1}{8}$ to $\frac{1}{50}$ without causing perceptible variation in the E. M. F.

THE DANIELL CELL.

The invention of this cell is ascribed by M. Tommasi to Becquerel, who in 1829 combined zinc, a neutral saline solu-

FIG. 80.—DANIELL CELL.

tion, a porous partition, a solution of copper nitrate or sulphate and copper. In 1830 Wach, desiring to study the endosmose of liquids and the precipitation of metals by the voltaic current, constructed an analogous apparatus consisting in a vessel divided into two compartments by an animal mem-

brane, one compartment containing a solution of ammonium chloride, or simply water, and a zinc plate, and the other a solution of copper sulphate and a copper plate.

The Daniell cell of 1836 (Fig. 80) consists of zinc, solution of zinc sulphate; porous cup, solution of copper sulphate, copper. Its E. M. F. is given as follows:

E. M. F.	Author.
1.058 volts *.	Fleming-Jenkin.
1.059 "	Favre.
1.059 "	Kittler.
1.079 "	Clark & Sabine.
1.084 " †.........................	D. Tommasi.
1.1015 "	Ledeboer.
1.155 " ....∴	Everett.
1.160 " ‡.........................	D. Tommasi.

When the zinc sulphate is replaced by dilute sulphuric acid, the E. M. F. is found as follows:

E. M. F.	Authors.
1.079 volts..	Clark & Sabine.
1.084 " †.........................	D. Tommasi.
1.110 "	Latimer Clark.
1.120 "	W. Thomson.
1.138 "	F. Kohlrausch.
1.140 "	Kittler.

With the zinc sulphate replaced by other saline solutions (Petrouchoffsky, 1858):

	Amalgamated Zinc.	Ordinary Zinc.
Solution of sodium chloride.........1.134 volts.		1.090 volts.
" " potassium tartrate..... 1.534 "		1.06 "

Chemical Reactions.—In the exterior vessel there is produced zinc sulphate and hydrogen, but the latter, instead of being disengaged, is carried to the copper sulphate and decom-

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* Calculated according to the heat developed in the chemical reaction.
† Calculated on the method of thermic constants.
‡ Calculated by electro-chemical equivalents.

poses it with the formation of sulphate of hydrogen (sulphuric acid) and metallic copper.

E. M. F.'S OF CELLS OF THE DANIELL TYPE. (E. REYNIER, 1884.)

Liquids.		E. M. F.'s in Volts.	
Copper Compartment.	Zinc Compartment.	Zin ^{Hg}	Zinc.
Saturated sol. copper sulphate	Solution zinc sulphate †	1.079	1.068
" " " "	Acidulated sol. zinc sulphate ‡	1.105	1.06
Acidulated " " " *	Solution zinc sulphate	1.03	1.025
" " " "	Acidulated sol. zinc sulphate	1.066	1.03
Saturated " " "	Solution sodium chloride §	1.145	1.14
Acidulated " " "	" " "	1.115	1.09
" " " "	Acidulated sol. sodium chloride ‖	1.125	1.09
Saturated " " "	Acidulated water (sulphuric) ¶	1.134	1.05
Acidulated " " "	" " "	1.119	1.027
Saturated " " "	Porous partition **	1.10	1.04
Acidulated " " "	" " **	1.05	1.04

* By addition of $\frac{1}{10}$ of monohydrated sulphuric acid.

† 500 grams of zinc sulphate per 1000 of water.

‡ $\frac{1}{10}$ sulphuric acid.

§ 200 grams sodium chloride per 1000 of water.

‖ $\frac{1}{10}$ sulphuric acid.

¶ $\frac{1}{10}$ sulphuric acid.

** The zinc electrode is simply immersed in the cupric liquor with its partition of parchment paper.

There is therefore in the external vessel

$$Zn + SO_4H_2 = SO_4Zn + H_2,$$

and in the porous cup

$$SO_4Cu + H_2 = SO_4H_2 + Cu.$$
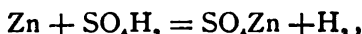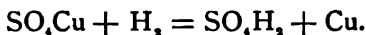
Endosmose.—In this cell there is a transport by the current of the exciting liquid into the porous cup, and the level of the sulphate of copper solution rises when the circuit is closed. There is, on the other hand, a transport of the cupric solution into the exterior vessel on open circuit.

Varley has proposed a means of preventing the transport of the copper through porous partitions, which consists in sur-

rounding the porous cup with a layer of zinc oxide. The sulphate of copper which penetrates into the mass of zinc oxide forms zinc sulphate and deposits the copper oxide in powder.

Incrustation of Porous Cups.—Incrustations of porous cups due to reduced copper, when this does not render them too impermeable, are advantageous owing to the intensity of the current produced; but, on the other hand, they cause a greater expenditure of copper sulphate. (Du Moncel, 1860.)

The incrustations of the porous cups are hindered by placing thereon a copper wire wound in a helix and terminating by a spiral plate which is applied to the bottom. The middle portion of the helix is connected with the copper electrode. (Bourseul, 1857.)

Effect of Temperature, Light, Dilution, etc., on the E. M. F. of the Daniell Cell.— *Effect of Temperature*—W. H. Preece has found that while the E. M. F. of this cell undergoes but slight modification under changes of temperature, its internal resistance is greatly affected. Sabine has reached the same conclusion and has obtained the following results:

Temperature.	E. M. F.
18°................	1.08 volts.
22	1.07 "
100	1.09 "

Nevertheless, Crova finds that the E. M. F. of the Daniell cell decreases regularly as the temperature augments. The experiments of M. Bouty were made to determine the thermoelectric E. M. F.'s at the contact of a metal and a liquid. He found that the E. M. F., when a copper plate in a cupric solution was employed, is for 1° C. equal to 0.000688 of that of a Daniell cell, and that it is rigorously proportional to the difference of temperatures of the two plates. This same proportionality was observed with platinum, amalgamated zinc, cadmium, mercury, gold, and iron, when immersed in their respective salts. The following figures, representing the average E. M. F. developed and due to the difference of one degree

between the temperatures of the two immersed plates, were thus obtained:

Platinum......................	0.000735
Copper	0.000696
Zinc..........................	0.000705
Cadmium	0.000616
Mercury	0.000140
Gold..........................	0.000024
Iron........	0.000002

It will be observed that the E. M. F.'s of copper and zinc are nearly equal; whence M. Bouty reaches the conclusion that the E. M. F. of the Daniell cell remains constant whatever may be the temperature to which it is subjected. Raoult (1863), however, finds the E. M. F. constant only between temperatures of 10° and 50° C.

The conflicting nature of the results obtained thus far, renders further investigation on this subject desirable. It is safe, however, to regard the E. M. F. of the Daniell cell as varying, under temperature changes, to such an extent as to make the cell doubtful as a standard for measurements intended to be accurate to $\frac{1}{1000}$ of its E. M. F.

Effect of Light.—A Daniell cell of which the copper is clean appears to be entirely insensible to light, but this does not hold true when the surface of the copper is altered by oxidation or by the formation of salt thereon. A cell the E. M. F. of which is equal to 1.5 volts, when exposed to sunlight loses about $\frac{1}{40}$ of its value (0.029 volt). This phenomenon is not due to an elevation of temperature, for the immersion of the cell in water at 50° C. does not produce any sensible effect. On the other hand, it has been noted that the more refrangible rays are those which act.

A sensitive Daniell cell can also be made by taking as the positive electrode a copper wire oxidized in the flame of the Bunsen burner. But in this case there is an increase of electromotive force due to the action of light. On putting a

similar wire into a solution of copper sulphate and completing the cell by a non-oxidized copper wire, it is clearly shown that sunlight renders the oxidized copper more positive. (H. Pellat.)

Effect of Dilution.—Regnauld (1855) has observed for the cell (zinc, zinc sulphate)–(copper sulphate, copper) that there is not much difference in the E. M. F. of the cell whether a concentrated solution of sulphate of zinc be employed or one one hundred times diluted with its volume of water. The same holds true on varying the degree of dilution of the sulphate of copper.

Regnauld has determined the following values: saturated solution of copper sulphate, 0.961 volt; the same diluted with twice its volume of, water, 0.961 volt; the same diluted with ten times its volume, 0.956 volt; with fifty times its volume, 0.945 volt.

In practice it has been found that, in order to obtain a zinc sulphate solution with maximum conductibility, it is necessary to mix one volume of a saturated solution of sulphate with one volume of water, the density of the solution being about 1.10.

Kittler has studied the variations of E. M. F. of the Daniell cell in which the copper is surrounded by a saturated solution of cupric sulphate and the amalgamated zinc with dilute sulphuric acid of density varying from 1.357 to 1.075. He has found maximum E. M. F. using acid of density of about 1.2.

Effect of the Condition of the Metals.—If in the Daniell cell (zinc, zinc sulphate)–(copper sulphate, copper) there be employed rolled copper or crystalline electrolytic copper roughened or burnished, or electrolytic zinc, crystalline or pulverulent, or finally amalgamated zinc, the E. M. F. is the same in all cases within $\frac{1}{100}$, provided it be determined always when the metals are well moistened. (F. M. Raoult, 1869.)

Caustic Potash and Bromine Elements.—According to Koosen, when caustic potash is employed in a Daniell cell instead of acid, its action is as follows: 1. KHO is decomposed, giving K, O, and water. 2. K replaces zinc, forming

sulphate of potash instead of sulphate of zinc. 3. Zn is oxidized by the liberated oxygen. 4. The zinc oxide thus formed is dissolved into the undecomposed KHO solution. Of these four reactions, (1) diminishes the E. M. F., (2) and (3) strengthen it, as possibly does (4). The E. M. F. obtained in practice agrees well with theory. A Daniell cell made up with tolerably strong caustic potash remains very constant on a high external resistance. Caustic soda answers still better, as it dissolves the zinc oxide more freely. It is important to avoid diffusion as much as possible, and for this purpose Herr Koosen prefers to employ two porous pots, one inside the other, with the space between filled with a solution of sulphate of soda or potash respectively.

Effect of Surface of the Electrodes.—According to Daniell (1838), when in his cell the zinc surface is augmented the intensity of the current remains nearly the same, while it becomes greater when the surface of the copper is increased. Du Moniel has also reached the same conclusion. " Thus," he says, " with the Daniell cells instead of diminishing the copper plates to a simple wire immersed in the sulphate of copper solution, they are better made in the form of copper cylinders as large as possible in order to increase in this way the dimensions of the elements and proportionately to reduce the surface of the zinc. Thus, while the resistance of the cell is not sensibly modified, the cell is rendered more constant, the expenditure of zinc less, the maintenance easier, and the saline efflorescence much diminished. With regard to the zincs, there is no advantage in making them of large surface unless the cell is required to have high intensity and long duration. When the zinc is attacked only on closed circuit, the weight of metal dissolved is the same whatever may be the surface of the zinc employed."

Effect of Amalgamation.—Amalgamation is useless when the zinc is immersed in a sulphate of zinc solution ; and the same is true when the liquid is dilute sulphuric acid or even ordinary water, since zinc sulphate is quickly formed. It has even been considered that the non-amalgamation of the zinc

favored the durability of the Daniell cell, because of the action of the mercury on the copper deposit formed on the zinc. It may be noted, however, that the London Post Office prescribes amalgamation of the zinc in its sulphate of copper standard cell, that Kittler also in his standard uses amalgamated zinc and that other electricians have found it of advantage to amalgamate the metal in various cells of the Daniell type.

Effect of Porous Diaphragms.—The most widely differing materials may be used as porous partitions in cells of the Daniell principle without modification of the E. M. F. Regnauld has tested partitions of unbaked porcelain, ebony, boxwood, and pipe-clay.

Effect of the Liquid interposed between the Saline Solutions of the Daniell Cell.—Raoult (1863) has made the following experiment. A series of drinking-glasses in contact is arranged. The extreme glasses of the series contain respectively copper with copper sulphate, and zinc with zinc sulphate. The intermediate glasses contain various liquids which may be changed as desired. The contiguous glasses communicate by inverted U-tubes which are filled with conducting liquids and closed by parchment-paper. The intermediate liquids used have been—solutions of copper sulphate; potassium sulphate; ammonium sulphate: aluminium sulphate: potassium nitrate: potassium chloride: ammonium chloride and zinc chloride. Acidulated water: water alkalinized by KHO: ordinary water: nitric acid: ammonia: mercuric chloride: ferrous sulphate: zinc sulphate: platinum chloride and ammonium sulphate. It was determined that the E. M. F. of the element remained the same no matter what liquids were interposed between the saline solutions in which the metals were immersed.

The Daniell Cell as a Standard.—*Constancy of the Daniell Cell considered as a Standard.*—It appears from the researches of Raoult (1863):

1. That the E. M. F. of the Daniell cell (copper, copper sulphate : zinc sulphate, zinc) remains the same whether the solutions be concentrated or diluted with more than 20 volumes of water.

2. That it is independent of temperature between 10° and 50° C.

3. That it is independent of the resistance of the cell between 2 and 30,000 ohms.

4. That it is the same whether the solutions be aerated or not.

5. That it is the same after two minutes or after a day of immersion of the copper or the zinc.

6. That it is the same whether the zinc be pure or amalgamated.

7. That it hardly varies when 25 per cent of zinc sulphate is mixed with the copper sulphate when commercial zinc or copper is used.

Kittler's Standard Daniell Cell (1882).—Kittler gives the name of " normal element " to a cell composed of chemically pure amalgamated zinc, in sulphuric acid of density 1.075 at 18°, and chemically pure copper in a concentrated solution of copper sulphate of density 1.19.   In these conditions the E. M. F. of this cell increases with the percentage of acid to a maximum corresponding to 25 to 30 per cent of acid. This augmentation is greater as the solution of copper sulphate is weaker, and attains its maximum with pure water.   It has been found, furthermore, that if very weak acids be used, the E. M. F. decreases with the degree of dilution of the copper sulphate ; from this it appears that there should exist a degree of concentration of the acid for which the cell should give the same E. M. F. whatever may be the degree of concentration or dilution of the copper sulphate.   The solution in question has the density 1.0011 at 16°.

Fleming's Standard Daniell Cell (1885).—This standard is composed of a U-tube containing in its branches a solution of copper sulphate and a solution of zinc sulphate; the two solutions being of the same density.   An electrode formed of copper freshly deposited by electrolysis is immersed in the copper sulphate solution ; the other electrode is a rod of chemically pure zinc immersed in a solution of zinc sulphate. The E. M. F. is 1.102 volts when the solutions are of similar

density. If, however, copper sulphate of density 1.1 and zinc sulphate of density 1.4 are used, the E. M. F. is 1.072 volts.

Standard Daniell Cell of the London Post Office.—Old Model. This consists of a box enclosing three separate vessels. The vessel on the left contains a plate of zinc immersed in water; that on the right receives a flat and rectangular porous cup which is immersed in water and contains a plate of copper. These two vessels are used only when the cell is at rest. The middle vessel contains a 50 per cent saturated solution of zinc sulphate, and at the bottom a little cylinder of zinc disposed in a special compartment. When the cell is to be used, the porous cup is removed from its vessel and is placed together with the zinc in the middle vessel. The cell is then ready. The small amount of copper sulphate which traverses the porous cup during the operation is deposited upon the zinc cylinder at the bottom of the middle vessel. The solution therefore remains very clear. E. M. F. = 1.079 volts. In constant use, the Post Office reckons its E. M. F. at 1.07 volts.

New Model. This is composed of two compartments. One contains a flat porous vessel in which are a plate of copper and crystals of copper sulphate. The porous cup is thus isolated when the cell is not in operation. The other compartment is filled up to a certain level with a 50 per cent saturated solution of zinc sulphate, and also contains the zinc plate. A pencil of the same metal is placed at the bottom of this compartment immediately below the zinc plate. When this cell is to be used, the porous cup is removed from its compartment and placed in the other compartment with the zinc; the level of the sulphate of zinc solution is thus raised so that the plate is wet. The cell is then ready. When the measurements are finished the porous cup is replaced in its compartment, and during the period of rest all the copper sulphate which has become mingled with the exciting solution of zinc sulphate is deposited on the cylinder. The solution thus is kept quite clear. E. M. F. = 1.07 volts.

Sir William Thomson's Standard Daniell Cell.—A glass jar has at its bottom a plate of zinc in a saturated solution of zinc

sulphate. The copper plate is suspended above. Copper sulphate half saturated is introduced through a funnel connecting by a rubber tube to a siphon which terminates in a pointed horizontal tube at the surface of the zinc sulphate. By filling the funnel and gently raising it the copper sulphate will flow over the surface of the saturated zinc sulphate so that the surface of separation between the two liquids will be clearly defined. Upon the termination of the experiment the funnel is lowered and the solution is run out. The cell should be used but once. E. M. F. at 15° C. = 1.072 volts. Temperature coefficient not accurately determined.

Lodge Standard Daniell Cell (Fig. 81).—Two glass tubes receive the two electrodes. The one which contains the zinc rod is open at both ends but constricted at its lower portion. This tube enters dilute sulphuric acid, which thus excites the metal. The copper sulphate solution is contained in the other tube, which is closed below and hence separated from the exciting liquid. (The tube is closed like the bottom of an ordinary test-tube.) The copper electrode enters the copper sulphate solution and consists of a wire covered at its upper portion with gutta percha and provided at its end with a deposit of electrolytic copper. Of course with this arrangement circulation of the current within the cell is impossible. In order to establish it, the

FIG. 81.

tube containing the zinc and the test-tube bottom containing the copper solution are united, and the moisture which covers the glass serves as conductor for the circuit. By this device the liquids are wholly prevented from mixing. The internal resistance of the cell at the same time is enormously increased,

which is necessary in order to maintain constant the E. M. F. during prolonged closing of the circuit. If dilute sulphuric acid of a density of 1.075 at 18° and a solution of copper sulphate of density 1.2 be used, the E. M. F. is 1.182 volts, which increases at the rate of 0.02 per cent per degree centigrade.

Beetz Standard Daniell Cell.—This cell consists of a U-tube 4 mm. in diameter. The arms are 22 cm. long and are equal. In one arm is introduced a paste of finely ground alabastrite and a concentrated solution of zinc sulphate, into which paste a zinc wire enters. When the paste has become solid there is placed in the other arm of the tube another paste of alabastrite mixed with a saturated solution of copper sulphate and containing a copper wire. This is, therefore, a dry pile. The E. M. F. is about 0.0027 volt less than that of the Daniell cell. Effect of temperature: 0° to 20°, 0.015 per cent for each centigrade degree; 20° to 40°, 0.053 per cent for each centigrade degree. On closed circuit this cell loses 0.005 volt after 10 minutes, 0.01 volt after 20 hours. For other standard cells see those of *Latimer-Clark, Regnault, Warren de la Rue, Ayrton and Perry, E. Reynier, Carhart, Edward Weston,* etc.

Cells of the Daniell Type.

Parelle and Vérité Globe Cell (Pile à ballon).—Zinc, solution of zinc sulphate or acidulated water; porous cup, solution of copper sulphate, copper. Above the porous cup as shown in Fig. 82 is a glass globe or flask filled with crystals of sulphate of copper and water. The neck of the globe enters the porous cup, and as the sulphate of copper solution is heavier than water, the solution in the porous cup is kept replenished or is resaturated as fast as it is weakened by deposit of the copper. The current from these globe cells, according to Du Moncel (1872), becomes notably weakened. Valencourt suggests, as the best means of maintaining uniform saturation of the copper sulphate solution, the addition thereto from time to time of a little copper carbonate.

FIG. 82.—GLOBE CELL.

Raoult Cell.—This consists of two vessels, V V' (Fig. 83), connected by a large curved glass tube T closed at the ends by porous plates. One vessel contains zinc and zinc sulphate, the other copper and copper sulphate.
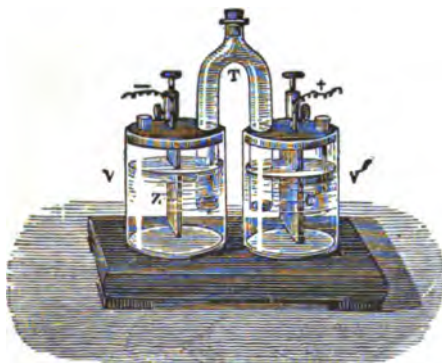
FIG. 83.—RAOULT CELL.

Eisenlorh Cell (1849).—Zinc, solution of sodium or potassium bitartrate; porous cup, copper sulphate solution, copper.

Buff Cell (1853).—Liquid zinc amalgam, solution of zinc sulphate; porous cup, solution of copper sulphate, copper.

The zinc electrode is a wire the lower end of which enters a body of mercury.

Gaiffe Cell.—In order to reduce the expenditure in the Daniell cell on open circuit, A. Gaiffe has devised the apparatus represented in Fig. 84. This consists of a glass containing
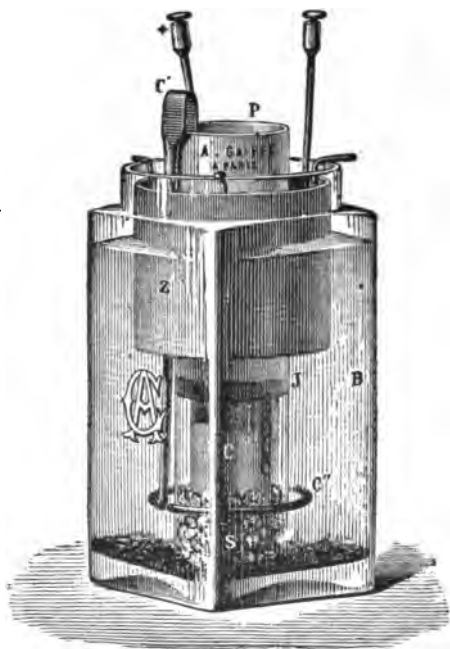
FIG. 84.—GAIFFE CELL.

vessel, *B*, an amalgamated zinc cylinder *Z*, suspended by hooks from the edges of the mouth of the jar, a cylinder, *P*, porous from *P* to *J* and terminating at its lower portion in a glass vessel, and finally a copper, *C*, which extends entirely up through the cylinder *P* and has an appendix, *C'C''*, which extends, as shown, nearly to the bottom of the jar *B*. The two vessels are filled with a saturated solution of zinc sulphate or magnesia diluted with its volume of water. Some sulphate of copper crystals are placed in *P*. The cupric solution rises as far as *J*, but can go no further as it then percolates

through the porous part of the cylinder and runs to the bottom of jar *B*. When this cell is placed in closed circuit, the action takes place first between C'' and Z and reduces the copper sulphate which has entered *B*. The cell then acts like one of the ordinary Daniell type between C and Z. The advantage claimed for this construction is that the zinc, being in a liquid free or very nearly free from copper sulphate, is not acted upon and used up while the cell is at rest.

Remark Cell (1862).—Small plates of zinc and copper are superposed and separated by plates of clay and by two disks of moistened wool. The disk on the zinc side is wet with dilute sulphuric acid; that on the copper side with copper sulphate. This cell is designed for medical uses.

F. Carré Cell (1869).—Zinc, solution of zinc sulphate acidulated with $\frac{1}{30}$ H_2SO_4, to which is added $\frac{1}{10}$ its volume of saturated solution of ammonium chloride; cup of albuminized or parchment paper, solution of copper sulphate, copper. Paper diaphragms were employed earlier by Frascara (1854), and then by Jedlick and Csapo (1855).

Watson Cell. (Fig. 85).—This contains an inverted lead funnel pierced with numerous holes and enclosing sulphate of copper crystals. The annular zinc is suspended from the cover. A solution of zinc sulphate and lead acetate is used in the proportion of sulphate 112 grams and acetate 56 grams. "The function of the lead acetate is to keep the metallic surface of the lead funnel in condition to receive the deposit of metallic copper with which it will become coated," so that the funnel acts as the negative electrode. It is connected to the binding post by a copper strip.

Fig. 85.—Watson Cell.

F. Carré Cell (1888), *Second Model.*—Each cell (Fig. 86)

consists of a glass vessel at the bottom of which is a wooden cross upon which rests a zinc cylinder. Projections on the cross enter recesses in the zinc and hold it in place. The negative electrode is a tube of red copper which rests on a porcelain cup, which acts as the bottom of a vessel made of parchment-paper of like diameter, to which it is firmly attached by a cord lacing or binding. On top of the copper tube is a disk of vulcanized fibre, around the edge of which are recesses corresponding to similar recesses made in the bottom of the porcelain cup. A single cord laced to and fro in these recesses holds the copper tube firmly in the centre of the cylinder of parchment-paper. The cell is set up in the following manner: The copper tube is first filled with copper sulphate; there is then poured into the glass vessel up to the top edge of the zinc a solution of zinc sulphate at 2° to 25° B., and water is put into the copper tube until it reaches the same level in the vessel of parchment-paper as that attained by the zinc sulphate solution.

FIG. 86.—CARRÉ CELL.

This cell gives the following constants:

1. Large model: E. M. F. = 1.07 volts; $I = 15$ to 25 amperes; $R = 0.07$ ohm; height of zinc = 48 cm.; diameter of zinc = 14 cm.

2. Small model: E. M. F. = 1.07 volts; $I = 8$ to 12 amperes; $R = 0.13$ ohm; height of zinc = 24 cm.; diameter of zinc = 14 cm.

Sir W. Thomson Cell.—Square trough in which is a copper plate, the area of which is nearly equal to that of the bottom of the trough; above the copper plate is copper sulphate solution. A zinc electrode, in the shape of an inverted grid, is placed above the copper plate and is supported on

four wooden rods. The zinc is enveloped below and on the four sides in a leaf of parchment-paper in which is placed pure water or a, solution of zinc sulphate. The cells are
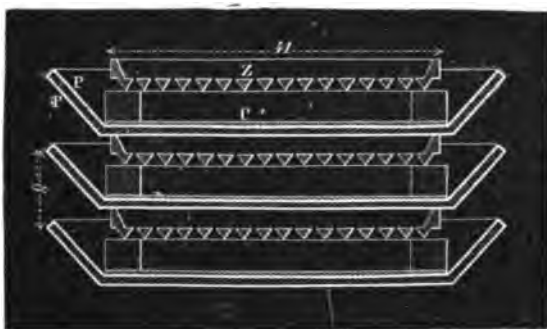
FIG. 87.—THOMSON BATTERY.

arranged in battery by being disposed one above the other (Fig. 87). The resistance of this cell is very small. It is used in submarine telegraphy for operating the siphon recorder.

O'Keenan Cell (1887).—This cell is automatic in its action. It differs from all other sulphate of copper cells in the arrangement, distribution, and automatic circulation of its liquids, and is so regulated that the latter enter and leave the cell without attention in proportion as work is demanded, and that the consumption of zinc and copper sulphate is simply that required for the work. Fig. 88 is a section of the cell. At *pb* are shown two plates of lead, immersed in a solution of copper sul-

FIG. 88.—O'KEENAN CELL.

phate. In the middle of the containing vessel is a tube of parch-

ment-paper open at its ends and receiving the zinc electrode and zinc sulphate. The upper part of this tube enters pure water; the lower part is immersed in concentrated zinc sulphate at the bottom of the containing jar. When circuit is closed a formation of zinc sulphate takes place in the porous tube throughout its length, due to the attack of the zinc, and at the same time there is a deposit of copper sulphate on the lead plates in the copper sulphate compartment. The zinc sulphate increases the density of the liquid in the tube, which accordingly descends, and as a consequence pure water enters the top of the tube and the heavy zinc sulphate escapes at the bottom. As long as the cell is in operation there is circulation of water and dissolved zinc sulphate, but when the circuit is interrupted the circulation ceases and expenditure of material stops. Fig 89 is a general view of a battery of ten cells in series, designed for charging a series of three accumulators. The ten cells are enclosed in an oblong trough of paraffined wood, the front of which consists of glass that permits the state of the battery to be seen at any moment. The dimensions vary with the discharge to be obtained and the number of the lamps. The model of medium size, here shown, is about four feet in height. The trough is divided into ten parts by wooden partitions. The front of each cell contains a vertical slit designed to establish a communication between it and the space in front. At the left end there is a rectangular box containing small apertures and terminating above in a hopper, *T*, that permits of filling it with sulphate of copper. It will be seen that the water in the trough, on circulating through the apertures, comes into contact with the crystals and fills all the cells with a saturated solution of sulphate of copper. In each cell there is a plate of zinc of very large size, enclosed in a sheath of parchment-paper, and the sides of the box are provided with two lead plates upon which is deposited the copper formed by the reduction of the sulphate, while the denser sulphate of zinc formed falls to the bottom of the cells.

On allowing water to enter the upper part of the battery,

drop by drop, three distinct and clearly separated strata are obtained. The first of these, which is of pure water, is but a fraction of an inch in thickness. The thickest is formed of sulphate of copper, and is of the blue color that characterizes that salt. The third, which is yellowish, is a saturated solution of sulphate of zinc. In order to have a continuous operation, then, it suffices to introduce water into the battery through the
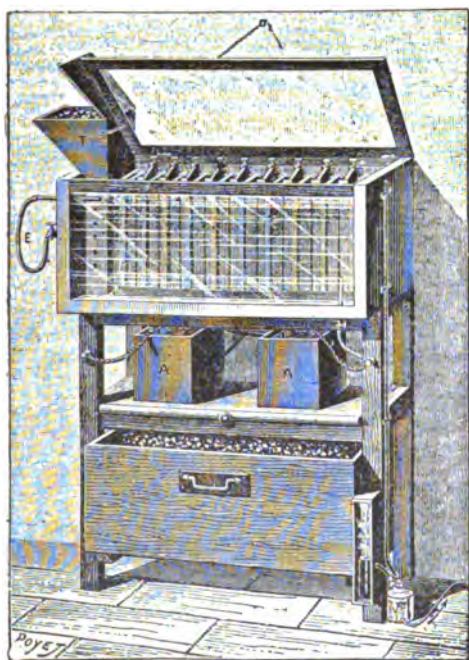
FIG. 89.—O'KEENAN BATTERY.

regulating cock, which is adjusted once for all. The excess escapes through the waste-pipe.

When the stratum of saturated sulphate of zinc has reached a certain thickness, it descends in a vertical tube arranged at the lower part of the box. The lower extremity of this tube enters a small reservoir containing mercury. The mercury thus has its level changed through the pressure of the column of sulphate of zinc, increased by that exerted by the stratum

of sulphate of copper and water. The height of the mercury above the lower extremity of the tube is regulated so as exactly to balance the column of zinc sulphate when the level of the latter reaches a certain point.

When the level of the zinc sulphate tends to rise as a consequence of the battery's operation, the solution then escapes from the lower part of the tube, rises above the mercury, and flows through a waste-pipe into a vessel that receives the excess of water. At the time of mounting, if care be taken to put in sufficiently thick zinc plates, a battery is obtained that is claimed to be capable of furnishing, without interruption, a constant current for several months.

D'Arsonval Cell (1881).—Zinc, soda solution; porous cup, sulphate of copper solution, copper. E. M. F. = 1.5 volts. · In this cell cupric hydrate (an insoluble compound) is formed in the pores of the porous cup, which hinders the mixing of the copper solution with the liquid of the exterior vessel. D'Arsonval has devised other cells on the same principle.

E. Reynier Cell.—Zinc^{Hg}, 30 per cent solution of caustic soda; seamless porous cup of parchment-paper, solution of copper to which is added sodium bisulphate or sulphuric acid. E. M. F. = 1.5 volt. Reynier has also employed in this cell the following solutions :

Exciting liquid: ordinary water 1200 parts, caustic soda 200, caustic potash 100, potassium chlorate 20, sodium chlorate 20, potassium sulphate 20, sodium sulphate 20.

Depolarizer : ordinary water 1200 parts, copper sulphate 240, nitrate of copper 60, potassium chlorate 20, sodium chlorate 20, potassium chloride 20, sodium chloride 20, zinc chloride (sat. sol.) 20, potassium sulphate 20, sodium sulphate 20, zinc sulphate 20.

Grove Cell.—Iron, salt or acidulated water ; porous cup, solution of copper sulphate, iron. The iron (last named) becomes covered with copper and hence acts as a copper electrode.

Ryhiner's Cell (1848).—Cast iron, salt water ; porous cup, sulphate of copper solution, lead. The exterior vessel is of iron. The copper sulphate solution is contained in a cylinder of

coarse cloth covered with three or four layers of paper. The lead becomes covered, like the iron in Grove's cell, with a coating of copper, and so acts as a copper electrode.

Trouvé Moist Cell (1884) (Fig. 89).—Each element consists
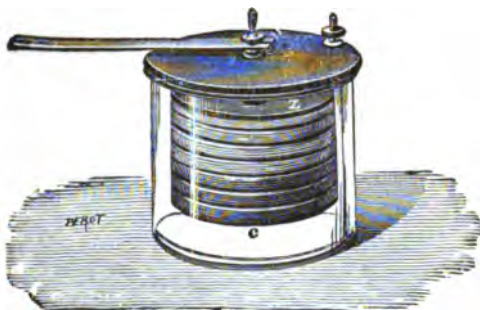
FIG. 89.—TROUVÉ CELL.

of a disk of zinc and a disk of copper, between which are several disks of blotting-paper half of which are wet with a solution of zinc sulphate and half with a solution of copper sulphate. When the cell is to be laid out of use the disks are allowed to dry in air; when it is needed, the disks are simply moistened. Another and simpler form of this cell is represented in Fig. 90. Here each couple consists of a glass tube filled with disks of blotting-paper impregnated as before and two disks respectively of copper and zinc placed at the ends of the paper column. The tube is closed at each extremity by a cork through which pass the wire terminals of the cell.
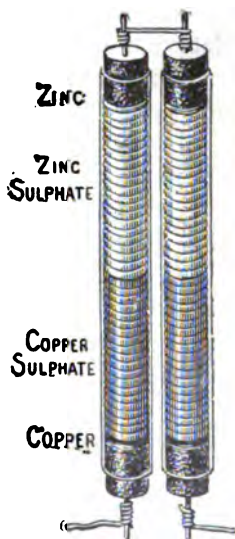
FIG. 90.—TROUVÉ CELL.

Siemens-Halske Cell.—The porous diaphragm is formed of compressed paper pulp saturated with salt to prevent mixture of the solutions and the unnecessary consumption of zinc and sulphate of copper. The outer vessel is of glass. The porous vessel is bell-shaped and receives a cross of sheet-copper,

above which it is filled with copper sulphate. **The paper diaphragm** encloses the lower part of the porous vessel and is quite thick, so that the cylindrical zinc rests upon its upper edge.

Kramer Cell.—In this cell separation of copper in the diaphragm is prevented by making the copper electrode in the shape of two perforated cylinders. One cylinder is placed inside and the other outside of the porous cup, the latter being filled with copper sulphate solution. Surrounding the outer copper cylinder is a porous tube, and outside of this tube again is the zinc cylinder.

The Trough Battery.—Two modifications of the Daniell cell are used in the English Telegraph Service, known as the Fuller and the Muirhead trough batteries. The battery is arranged in a rectangular box divided into compartments by slate partitions. Each compartment is again divided by a porous porcelain plate. One division contains a solution of copper sulphate and the copper plate, and the other a very dilute solution of zinc sulphate and the zinc plate. A zinc plate and a copper plate are joined by a copper strip which is bent so as to allow the plates to be supported by the intervening partition.

Guérin Cell (1884).—This is a portable variety of Daniell cell made by mixing the liquids with a hot solution of *agar-agar*, a sort of sea-weed found in extreme Oriental countries, which on cooling produces a solid and elastic jelly.

Gethin Cell.—This belongs to the gravity type, but contains a horizontal partition by which it is claimed that the action of gravity is assisted. The liquids thus have sharp lines of division and their intermingling is thus effectually prevented.

Fig. 91 shows the cell complete. The porous jar is provided with a rim which acts as a support, the whole resting on the upper edge of the glass jar. The zinc electrode rests on the bottom of the partition.

It is claimed that the use of the cell over extended periods has demonstrated that no filling of the pores of the partition with copper takes place, and that in several instances a year's

constant work was effected with a single charge of 4 pounds of copper sulphate and the consumption of 1½ pounds of zinc. The E. M. F. of the cell is 1.07, and its internal resistance about 3 ohms.

FIG. 91.—GETHIN CELL.

Kohlfurst Cell.—The containing vessel is a glass jar having a contraction at its lower part. The cover supports a conical plate of zinc. The other electrode is an S-shaped piece of lead in the bottom of the cell. Above the lead the cell is packed with copper sulphate crystals up to the contraction above noted. Above the contraction is a partition of unglazed earthenware. The exciting liquid is magnesium sulphate solution. E. M. F. = about 1 volt.

Sand Cells of the Daniell Type.—*Minotto Cell* (1863).— Copper, saturated solution of copper sulphate ; body of sand, zinc, solution of zinc sulphate or pure water. The zinc is in disk form and is laid flat on the sand. D'Arsonval replaces the sand in this cell with animal black, which holds the copper salt and prevents it depositing copper on the zinc. Coronat has substituted sawdust for Minotto's sand.

Jacobini Cell (1863).—Earthenware vessel at the bottom of which is a body of sand upon which rests a zinc cylinder like that used in the Bunsen cell. In the cylinder is an open tube of copper which enters the sand and which is filled with copper sulphate crystals. Water is added to the cell to set it in operation. Secchi, Calla, Candido, and others have also devised modifications of the Minotto cell.

Cells of the Daniell Type without Diaphragms—Gravity Cells.—Cells of the gravity type are especially useful where a light current is desired for continuous work, as in the operation of telegraph lines, fire-alarm signals, electric time service, small motors, etc., as great economy is shown in the amount of material consumed and in the care required for their maintenance. They are not suitable for ringing house-bells or for work of a similar character, owing to the number of cells required. Occasionally cells of the gravity type are coupled to secondary or storage cells and the stored energy afterwards used for various purposes, but except in special cases the economy of such action is questioned. The solution freezes at about 20 degrees Fahrenheit, so that care must be taken with the cell in cold weather, more especially as the internal resistance rapidly increases in all cells as the temperature of the fluid approaches the freezing point.

The E. M. F. is rated at 1.10 volts, and the internal resistance at 4 ohms, and, like the Daniell, the E. M. F. is nearly constant and not changeable as in many other cells. But it will not prove economical to obtain any but the lighter powers from gravity cells, as, the current strength being only about one half ampere and the normal E. M. F. about one volt per cell, the output of electric energy is about one half a watt, or

one fifteen-hundredth of a horse-power. In other words, it would require 1500 cells in circuit one hour to furnish one horse-power hour of electrical energy. (De Land.)

Meidinger Cell (1859) (Fig. 92).—The outer vessel *A* is contracted as shown at *b*. Upon the ledge thus formed rests the zinc cylinder *Z*, to which is connected the negative terminal *c*. A second smaller vessel *d* contains the copper or lead electrode *e*. The tube *h*, which is open at its lower end, contains copper sulphate crystals, which dissolve so that the copper sulphate solution, having the greater specific gravity, descends and surrounds the copper electrode, while the lighter magnesium sulphate solution remains in the upper part of the vessel.
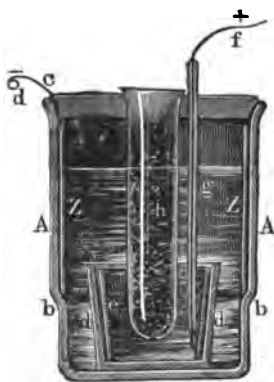
FIG. 92.—MEIDINGER CELL.

In order to reduce the precipitation of the copper on the zinc, J. Moser has proposed to suspend a band of zinc a few centimetres in length below the cylindrical electrode of that metal. The deposited copper from the sulphate will then rise no higher than this band and hence not reach the zinc cylinder, so that the effects of polarization are thus prevented. In the " globe " form of the Meidinger cell which is used in the Russian Telegraph Service and at the Mansfield Mines at Eisleben for the electrolytic extraction of copper, the tube holding the crystals is replaced by an inverted globular flask, which serves also as a cover for the containing vessel. E. M. F. = about the same as the ordinary Daniell cell.

Callaud Cell (1861).—Zinc, solution of zinc sulphate ; solution of copper sulphate, copper. The zinc is at the top and the copper at the bottom of the jar, as shown in Fig. 93.

Trouvé-Callaud Cell (Fig. 94).—At the bottom of the glass containing jar is a flat spiral of copper. The end extends vertically upward and is protected by a glass enclosing tube. The zinc is circular and is supported by projections from the

edge of the jar. On the spiral are placed copper sulphate crystals and water.
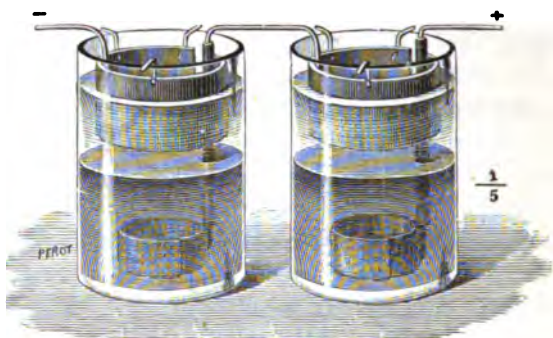
FIG. 93.—CALLAUD CELL.

Lockwood-Callaud Cell.—The zinc electrode is suspended from radial bars extending across the top of the vessel. One half of the jar is filled with copper sulphate crystals. The
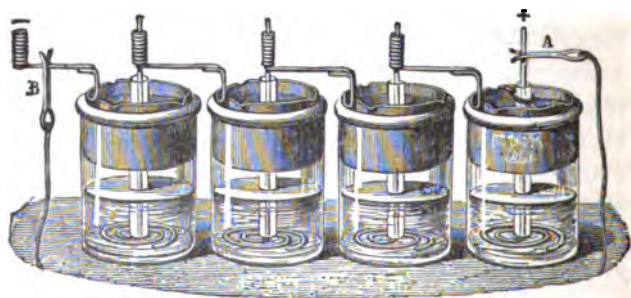
FIG. 94.—TROUVÉ-CALLAUD CELL.

copper electrode consists of two spirals, one at the bottom of the jar, the other resting on top of the crystals. The liquid is a solution of zinc sulphate. Evaporation is diminished by a floating layer of oil.

Western Union Standard Gravity Cell (Fig. 95).—This is an improved form of Callaud cell. The zinc is made with numerous openings and is vertically adjustable.

Vérité Cell (1863).—Glass jar filled with pure water and containing a cylinder of zinc in which is placed a copper vessel

the diameter and height of which are less than those of the exterior jar. The copper vessel is filled with crystals of copper sulphate, in which enters the neck of an inverted flask filled with similar crystals. Other modifications of the Daniell cell

without diaphragm have been made by Norman, Ubicini, Lockwood, Krüger, and others.

Thomson Cell.—In this cell the sulphate of zinc solution is below the copper sulphate solution, saturated solutions being used. (SO_4Zn. D = 1.44 and SO_4Cu. D = 1.18.) A cell based on the same principle was devised by Cardarelli in 1883.

Callaud Cupric Chloride Cell.—If in the Callaud cell cupric chloride be substituted for the copper sulphate, the E. M. F. decreases about one tenth, and the resistance considerably augments (Cailleret, 1877). A part of the chlorine from the cupric chloride unites with the zinc, forming zinc chloride and cuprous chloride,

$$2Cl_2Cu + Zn = Cl_2Zn - Cl_2Cu_2.$$
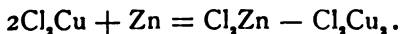
The decomposition of the water under the influence of the current produces at the same time zinc oxide, which in presence of the chlorides of zinc and copper gives oxychlorides of zinc and copper. Finally the hydrogen from this decomposition reduces the insoluble salts.

According to Lourme (1878) cupric chloride, especially in concentrated solution, attacks copper and produces cuprous chloride; but when the circuit is closed, cuprous chloride is not formed and a deposit of copper is obtained on the cathode. Chloride of zinc is formed, and on the zinc there is deposited a light precipitate which appears to be a mixture in variable proportions of Cu_2O and CuO. When the circuit is open, the cupric chloride attacks the copper electrode and forms cuprous chloride, which disappears when the circuit is closed.

Peclet Cell (1839).—A copper vessel containing a solution of copper sulphate in which is immersed a plate of zinc contained in a bag of strong cloth.

Delany Gravity Cell.—The sulphate of copper is enclosed in a strawboard box (Fig. 96). The zinc is in a paper envelope, and the rim of the jar has attached to it on the inside by a

FIG. 96.—DELANY CELL.

sticky substance a band of rubber cloth. The advantages claimed for the cell are as follows: When the battery is first set up, the dust of sulphate of copper is not instantly dissolved and diffused throughout the liquid, coating the zinc with copper, as is the case with the ordinary cell. Several minutes elapse before discoloration of the fluid begins, and then only at the bottom of the cell, from whence it rises very gradually, never reaching the zinc. If the box be filled the charge of copper is always uniform. Deposited or spongy metallic copper cannot fall upon the crystals from the zinc, and caking or massing in the bottom of the jar is thus prevented. The copper electrode is held firmly in position, and always at the same distance from the zinc. One zinc will endure two charges of sulphate of copper. The band around the rim is one of the most important features of the cell, as it prevents zinc sulphate from creeping over. It offers simply a mechanical obstruction.

Hussey Cell.—This consists of an outer glass jar; a copper disk ; a clay cup standing on four short legs and made porous only through the raised bottom surface, the sides being glazed to prevent any absorption above the lower edge ; and a four- wing plate of an amalgam of mercury and zinc that stands within the cup.

In charging this cell the space between the sides of the glass jar and that of the porous cup is partly filled with copper sulphate, and the latter is then covered with a weak mixture of sulphuric acid in water. This acidulated solution is also poured into the porous cup to a much higher level than in the glass jar, thus securing the advantage of a downward pressure that is always constant, and preventing the solution of copper from reaching the zinc. As the copper sulphate is consumed, it constantly feeds downward toward the bottom of the jar and porous cup, thus furnishing fresh solution to the active portion of the cell. E. M. F. claimed = 1.10 volts.

Crow-foot Cell.—The ordinary cell consists of a glass jar 6 inches wide by 8 inches high ; a form of copper cross is made by riveting three sheets of hard rolled sheet battery copper of No. 32 B. & S. gauge, 6 inches long by 2 inches wide, to a No. 16 B. & S. gauge copper wire covered with gutta-percha insulation, and a three-pound zinc is cast in a form resembling a crow's foot.

In setting up the cell, the copper strips are bent in the form of a Greek cross, and placed on the bottom, with the end of the wire overlapping the edge of the jar. The zinc is suspended on the opposite edge of the jar by the hook on the shank. Sufficient water is poured in to just cover the zinc, and about a pound of blue vitriol is dropped in, or a quantity sufficient to cover the copper cross, if steady, continuous work is desired. The wires are then connected and the battery allowed to stand for from 24 to 48 hours, when it will be ready for work. Or the action can be secured more quickly by adding a teaspoonful of sulphate of zinc to the water. But in the latter case it is best to add the blue vitriol to half a jar of water, then to dissolve the teaspoonful of sulphate of zinc in

sufficient water, and gently pour the same into the jar to within two inches of the top.   When the two solutions have properly separated, the lower of a deep blue color and the upper nearly colorless, then suspend the zinc in the jar, connect the wires, and it will soon be ready for service.   This avoids the deposition of copper that is always found on the zinc, and retards the action, when left in during the separation of the fluids.

No further attention should then be required until the need of a fresh supply of blue vitriol is shown by the receding of the blue color below the top of the copper cross ; or the replacing with fresh water of a portion of the upper fluid (solution of sulphate of zinc), when its specific gravity is indicated by a hydrometer to be 35 degrees or over.   A reading of 15 degrees or under indicates that the battery is growing weak through the absence of sufficient sulphate of zinc.   The transfer of the liquids should be carefully performed with the aid of a large battery syringe.   It should also be noted that as the blue color falls below the cross the internal resistance increases.

D'Infreville " Wasteless" Gravity Zincs.—There is a great waste of zinc in batteries, owing to the fact that the zinc electrode must be removed before it is entirely consumed, the current having become too weak on account of the increased internal resistance due to the diminished size of the zinc electrode.   This waste, in the case of the best patterns of zinc for gravity battery, often reaches forty-five per cent of the total weight of zinc purchased, $1\frac{1}{2}$ pounds being wasted out of $3\frac{1}{4}$ pounds of zinc.   In many places the stumps cannot be used to any advantage, nor sold, and it will not pay to gather and ship them to a place where they can be disposed of.   Even when collected, they can at best be sold only as impure metal at about half the price of spelter, so that in the most favorable case, where one half of the value of the stumps is recovered, the loss will still amount to about twenty-two per cent.

The invention illustrated in Figs. 97 and 98 consists in using for the zinc electrode a number of pieces adapted to be connected to one another in column by joints or connections which are liquid-tight or adapted to preserve the connecting

parts from the action of the battery liquid, so that a partially consumed piece may be connected or attached to the bottom of a fresh or new piece, which latter, after being partially consumed, and after the still greater state of consumption of the first one, may in its turn be connected underneath a new piece, and so on.

In time the lower piece of zinc will have been entirely consumed; then the one directly above it and to which it was attached, and so on, so that practically every piece of zinc introduced into the battery will in its turn be entirely consumed. This fact has been repeatedly confirmed by experience, and the electrode is therefore called the " wasteless " zinc. This arrangement and process are shown in perspective in Fig. 96, which represents one complete gravity element fitted up with the " wasteless " zinc electrode. This consists, first, of a new zinc piece suspended from a
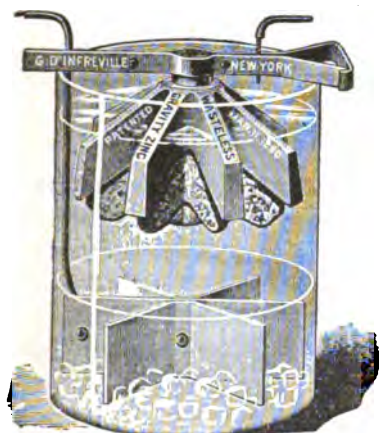
FIG. 97.—" WASTELESS " ZINC.

hanger resting on the rim of the jar so that the zinc dips about half-way into the sulphate of zinc solution; of a second piece of zinc partially consumed and suspended from the first one; and of a third piece or stump of zinc almost entirely consumed, and suspended from the second piece. The last two zinc pieces are entirely below the upper level of the battery solution. Fig. 98 represents the three pieces constituting the zinc electrode, showing their relative positions and comparative sizes, due to the state of corrosion of the two lower pieces, depending on the length of time they have been in use.

Corrosion of the Copper in Daniell Cells without Diaphragms.—It was formerly supposed that the corrosion of the copper in Daniell cells of this type was due to the action of the oxygen in solution on the water. The investigations, how-

ever, of A. Candeli and R. Velani (1883) indicate the following as the cause : The copper being immersed both in water and in a solution of copper sulphate forms of itself a couple in closed circuit.   Of this couple it is at once both the active and the inac-

FIG. 98.—" WASTELESS " ZINCS.

tive metal : active on the side of the water which it decomposes, inactive on the side of the sulphate.   The hydrogen disengaged through the decomposition of the water acts on the copper sulphate, and taking the place therein of the copper, produces sulphuric acid, which in turn attacking the copper oxide, reproduces the sulphate.   This reaction is expressed in the following equations :

1. $H_2O + Cu = CuO + H_2.$

2. $H_2 + SO_4Cu = Cu + SO_4H_2.$

3. $SO_4H_2 + CuO = SO_4Cu + H_2O.$

In order to avoid this corrosion it is useful to cover with gutta percha the copper rod which traverses the two liquids.

Cells Analogous to the Daniell.

Mauri Cell (1881).—Zinc, salt water to which from 1 to 2 per cent of potassium bichromate is added; porous cup, at the bottom of which is a body of flowers of sulphur, solution of copper sulphate containing crystals of that salt.   Plate of lead covered with a layer of sulphur obtained by immersion of the plate in a solution of potassium sulphide.   E. M. F. =

1.15 volts (open circuit) or 1.05 volts (closed circuit). According to Mauri, in this cell no copper deposit is formed either on the porous cup or on the zinc, which latter is not attached except in closed circuit.

Frascara Cell (1854).—Cast-iron vessel filled with water to which nitric or sulphuric acid is added; paper diaphragm (*xyloid*) ammonia and carbon. Xyloid paper is prepared with nitric acid and has similar properties to gun-cotton, including the ability to resist the action of acids.

Copper Sulphate Cell of the Leclanché Type.—In this cell the carbon of the Leclanché cell is replaced by copper in sulphate of copper, the zinc rod being in sal-ammoniac. There is a special modification in the porous pot itself, which is prepared by dipping it, to one third of its height, into melted paraffine wax, and then filling it with an aqueous solution of ammonia. The ammonia solution is then poured out and replaced by copper sulphate, which is in its turn removed, and, finally, the pot is allowed to drain dry. The object of this successive dipping into ammonia and copper sulphate solutions is the formation of a double sulphate of copper and ammonium which fills up the pores of the cell, and being insoluble in either of the solutions used in the battery, prevents them from mixing.

CHAPTER IX.

CELLS HAVING TWO LIQUIDS (*Continued.*)

I. CELLS HAVING DIFFERENT ELECTRODES.

(2) SOLID DEPOLARIZERS.

(a) Lead Peroxide (PbO$_2$).

IN 1843 Wheatstone observed that by covering the negative electrode of a cell with a body of peroxide of lead or peroxide of manganese, the E. M. F. of a cell could be greatly augmented. De la Rive reached the same conclusion at about the same period.

De la Rive Cell (1843).—Zinc^{Hg}, dilute sulphuric acid; porous cup, lead peroxide, platinum. E. M. F. = 2.4 volts. After thirty minutes of closed circuit, E. M. F. = 2.16 volts. With a positive electrode of iron, E. M. F. = 1.73 volts. The chemical reactions are represented by the following equations:

$$Zn + SO_4H_2 = SO_4Zn + H_2.$$

$$H_2 + PbO_2 = PbO + H_2O.$$

$$PbO + SO_4 H_2 = SO_4Pb + H_2O.$$
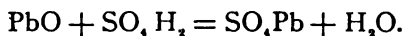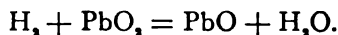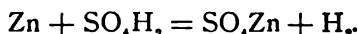
According to De la Rive, a single peroxide of lead cell decomposes water more energetically than the Grove cell of the same dimensions. This advantage is not maintained when several peroxide of lead cells are employed, for two lead peroxide cells give a much less powerful effect than two Grove cells; but if one Grove cell be connected to one lead peroxide cell, then more

·energetic effects will be obtained than with two peroxide cells, or even with two Grove cells. This is probably due to the high resistance of the peroxide cell, which is owing in great part to the presence of lead sulphate.

E. O'Keenan Cell (1883).—Zinc-carbon surrounded with lead peroxide, dilute sulphuric acid. E. M. F. = 2.2 volts. The lead peroxide is made into a paste with collodion, which is spread upon the carbon electrode.

Joule Cell.—Zinc^{Hg}, potash solution; porous cup, dilute sulphuric acid, lead covered with electrolytically deposited peroxide. E. M. F. = 2.544 volts.

Roberts Cell (1886).—Zinc^{Hg}-carbon surrounded with an agglomerate of lead peroxide, solution of sodium chloride to which is added a small quantity of sodium bichromate. E. M. F. = 1.8 volts. The agglomerate is made by adding together minium, powdered potassium permanganate, and sufficient hydrochloric acid to make paste. By the combined action of the permanganate and the acid, the minium, Pb_3O_4, is transformed into peroxide PbO_2. The paste is then introduced into a mould containing the carbon electrode, and when it is set, which happens after a few minutes, the mould is withdrawn and it is dried at the ordinary temperature. A mass almost as dense as carbon is produced. The bichromate is added to the exciting liquid in order to prevent the lead chloride which is contained in the agglomerate from dissolving and forming lead deposits on the zinc. The sodium bichromate transforms the slightly soluble lead chloride into completely insoluble lead chromate.

D. Tommasi and Radiguet Cell.—(See Cells having Identical Electrodes.)

(b) Peroxide of Manganese (MnO_2).

Leclanché Cell (1868).—Zinc, solution of ammonium chloride; porous cup, peroxide of manganese, carbon. E. M. F. = 1.48 volts.

A complete "disque" Leclanché cell (Fig. 99) consists of a

glass jar 6 in. $\times$ 4 in.; an amalgamated round or square zinc rod, 6 in. $\times$ ⅜ in., weighing about 3 oz., and a porous cup having in in the centre a carbon plate, 6 $\times$ 1½ in. $\times$ 5$\frac{1}{16}$ in., surrounded with manganese peroxide. The porous cup should be made of the best quality of white clay baked sufficiently to give the
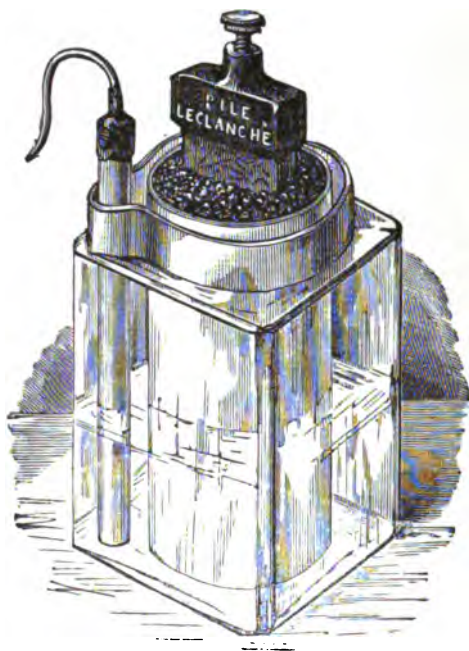
FIG. 99.—LECLANCHÉ " DISQUE" CELL.

proper degree of porosity, lack of which will prevent the absorption of the ammoniacal solution and increase the internal resistance. Only the best quality of manganese peroxide should be used free from all dirt and finer particles, and in clean pieces about ¼ in. in diameter. About 16 oz. are usually packed around the carbon, which with binding post attached is placed in the cup. Two small funnel-shaped glass tubes are disposed above the manganese, affording egress for the gas generated, and also admitting the small quantity of water or

sal-ammoniac solution that is added when immediate source is required. The top is then covered with a coating of paraffine and black wax.

The chief item of expense in this cell is the porous cup (with contents complete), which is seldom serviceable for a longer time than two years; the theoretical reduction of the peroxide of manganese, being at the rate of one grain to each half-grain of zinc dissolved and each grain of sal-ammoniac consumed, makes the ultimate cost of the cell oftentimes exceed the price asked for special forms of open-circuit carbon cells, which possess certain advantages and are supposed to last indefinitely, the zinc and sal-ammoniac only being occasionally renewed in each case, as in the " disque."

According to Leclanché, a concentrated solution of ammonium chloride should be used, because the zinc oxychlorides formed therein dissolve more easily than in a weak solution. In practice he has found that 100 grams of ammonium chloride correspond to 50 grams of zinc dissolved and to 100 grams of peroxide of manganese.

The use of peroxide of manganese as a depolarizer appears to have been first proposed in 1843 by De la Rive; but Leclanché seems to have been the first to use this depolarizer in a cell with an exciting solution of ammonium chloride. The ammonium chloride of commerce often contains relatively large quantities of sodium sulphate (5 to 7 per cent), as well as traces of iron. By comparative experiments with two zincs, one placed in a solution of commercial chloride and the other in a solution of the pure salt, a large difference in the duration of the cell has been determined. If the ammonium chloride be replaced by sulphate, double sulphates of zinc and ammonium are produced which are so little soluble that at the end of several hours' work the zinc becomes entirely covered with a crystalline deposit the resistance of which reaches several ohms. Ammonium nitrate is open to the same objections, although in less degree.

Leclanché has endeavored to replace the ammonium chloride with the chloride of potassium or sodium, but the results

which he has obtained have not been satisfactory, for the reason that no combustion of hydrogen takes place, or, if it does, it is excessively small. "This great difference," says Leclanché, "of combustibility between NH_4 (ammonium) and free hydrogen (coming from the decomposition of the water by the alkaline metal) in presence of manganese peroxide is so apparent that on disposing manganese peroxide in presence of an amalgam of sodium and of water, it has been impossible to perceive the formation of appreciable traces of the sesquioxides or lower oxides of manganese, while by substituting an amalgam of ammonium for amalgam of sodium, there is always an obvious reduction of the manganese peroxide."

The peroxide of manganese used should be very pure and a good conductor of electricity. The best is that which is known in commerce under the name of *manganese aiguillé* (pyrolusite). The peroxide is often used mixed with small fragments of retort-carbon or coke.

The Chemical Reactions in the Leclanché Cell are as follows: The zinc combines with the chlorine of the ammonium chloride and forms zinc chloride; ammonia is set free; the disengaged hydrogen with one part of the oxygen from the manganese peroxide forms water and transforms the manganese oxide into sesquioxide. This is represented in the following equation:

$$2ClNH_4 + 2MnO_2 + Zn = Cl_2Zn + 2NH_3 + H_2O + Mn_2O_3.$$
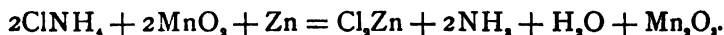
Through the secondary reactions there are formed oxychloride of zinc, double chloride of zinc and ammonium, nitrate of ammonium, and different gases. We will examine successively the mode of formation of these different products.

Zinc Oxychloride.—The presence of several oxychlorides has been noted, among which but two have a well-defined composition, namely, $Cl_2Zn(ZnO)_3$, 4 aq., and $Cl_2Zn(ZnO)_4$, 10 aq., both soluble in a saturated solution of ammonium chloride, but insoluble in pure water.

These two oxychlorides undoubtedly are formed in accord-ance with the following equations:

$$4Cl_2Zn + 6NH_3 + 7H_2O = Cl_2Zn(ZnO)_3, 4H_2O + 6ClNH_4.$$

$$7Cl_2Zn + {}_{,}2NH_3 + 16H_2O = Cl_2Zn(ZnO)_6, 10H_2O + 12ClNH_4.$$
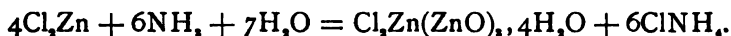
Chloride of Zinc and of Ammonium.—This chloride is formed in clearly-defined crystals on the zinc and on the porous cup cf the Leclanché cell. Analysis of these crystals made by different chemists has assigned to them the following formulæ:

$$3Cl_2Zn, 8NH_3, 4H_2O \text{ (Ferray)}.$$

$$Zn(OH)_2, ClNH_4 \text{ (Davis)}.$$

$$Zn(NH_3Cl)_2 \text{ (Divers)}.$$
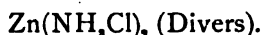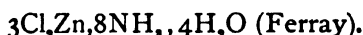
Ammonium Nitrate.—According to D. G. Fitzgerald (1877), considerable quantities of ammonium nitrate are formed in the Leclanché cell, in accordance with the following equation:

$$4NH_3 + 16MnO_2 = 2NO_3NH_4 + 8Mn_2O_3 + 2H_2O.$$

Composition of the Gas.—Analysis of the gas disengaged by the Leclanché cell shows, at the beginning of the action, hydrogen 0.5 volume, nitrogen and carbonic acid 0.5 volume; but after a prolonged closing of the circuit pure hydrogen only is evolved. (Ferray, 1875.)

Investigations of Divers (1883) on the Chemical Re-actions Produced in the Leclanché Cell.—I. *Action of the Zinc on the Ammonium Chloride.*—When the cell is cold this action is very weak; a little hydrogen is disengaged, the solution becomes alkaline, and the formation of ammonia and of the compound $Zn(NH_4Cl)_2$ is observed. This compound is dissolved in the ammonium chloride. On heating the cell, ammonia is disengaged. The compound $Zn(NH_4Cl)_2$ is de-stroyed, yielding zinc chloride. The compound of zinc and ammonium chloride is partially decomposed by the water and

yields an insoluble body having the composition OH–Zn–NH$_2$Cl.

II. *Action of the Ammonium Chloride on the Oxide of Manganese.*—Pure binoxide of manganese digested with a solution of ammonium chloride gives no reaction. The protoxide is slightly attacked cold, and more strongly when heated; ammonia is disengaged and manganese enters into solution. The intermediary oxides are equally attacked. The compound Zn(AzH$_3$Cl)$_2$ dissolved in NH$_4$Cl acts gradually on Mn$_2$O$_4$H$_2$ to give ammonium chloride and the body ZnO$_4$Mn$_2$.

III. *Action of Ammonium Chloride on Zinc and Manganese Binoxide.*—When chloride of ammonium is caused to act on zinc and manganese binoxide at the same time, hydrogen and ammonia are disengaged, and the solution becomes charged with zinc and manganese; the liquid deposits a substance which becomes brown on contact with the air. It is also observed that the binoxide is covered with a compound of zinc and manganese, soluble in ammonium chloride.

The theory of the Lelanché cell is as follows:

There is first the primary effect which by the action of Mn$_2$O$_4$ on NH$_4$Cl and Zn gives Mn$_2$O$_4$H$_2$, Zn(NH$_3$Cl)$_2$; then a secondary effect which polarizes the cell; Mn$_2$O$_4$Zn and Zn(NH$_3$Cl)$_2$ reacting furnish the compound Mn$_2$O$_4$Zn. In another secondary action which depolarizes the cell, this compound Mn$_2$O$_4$Zn is destroyed by ammonium chloride. There is a disengagement of ammonia and formation of MnO$_2$, MnCl$_2$, and Zn(NH$_3$Cl)$_2$.

E. M. F. of Polarization of the Leclanché Cell, in Accordance as the Carbon is in Fine or Coarse Powder.

	Time.	Fine Powder.	Coarse Powder.
E. M. F. of polariz. after 15 min......		0.324 volt.	0.088 volt.
" " " 30 "......		0.486 "	0.097 "
" " " 45 "......		0.540 "	0.118 "
" " " 60 "......		0.550 "	0.127 "

Annual Electric Work corresponding to a Deposit of Copper in a Sulphate of Copper Voltameter.

	R.	Copper deposited.
Small model, porous cup, 6 cm. diameter, 11 cm. high.......	9 to 10 ohms	40 grams
Average model, 6 cm. diameter, 15 cm. high................	5 to 6 "	60 to 70 "
Large model (disque cell) 8 cm. diameter, 15 cm. high........	4 "	100 to 125 "

Table showing Comparison between the Polarization of the Le-clanché Cell and the Clark and Muirhead Cell.

		Loss of E. M. F. due to Polarization.	
Resistance of the Circuit.	Time.	Leclanché Cell.*	Clark & Muirhead.
100 ohms	1 minute	1.5 per cent	1 per cent.
" "	5 minutes	5 " "	2 " "
" "	10 "	10 " "	4 " "

Continuation of the experiment shows that the Leclanché cell goes on falling while the other cell remains constant.

Modifications of the Leclanché Cell.—In the so-called " Gonda" form of the Leclanché cell (Fig. 100) the porous cup is not used, the depolarizer being made in the form of cakes or prisms attached to a carbon plate suspended in a solution of sal-ammoniac, the positive electrode being the usual zinc rod. The depolarizing substance used is said to have been composed of 52 parts of powdered carbon, 3 parts of bisulphate of potash, 40 parts of peroxide of manganese, and 5 parts of gum-lac resin, the latter being added to hold the component parts together. After being thoroughly mixed, the compound is exposed to a heat of 212 degrees Fahrenheit and then moulded into the desired shape under a pressure of 4500 lbs. to the square inch.

---

* On a resistance of 70 ohms a Leclanché-Barbier dry element of the smallest form, yielding 20 milliamperes at the beginning, gave 19.5 milliamperes at the end of an hour. For a new cell, therefore, the polarization was but 2.5 per cent.

The complete cell consists of a glass jar, with rubber top having grooves on the side permitting the escape of the gas formed within the cell, and two openings near the centre. An amalgamated zinc rod passes snugly through the smaller, while through the larger aperture a carbon plate should be fitted so
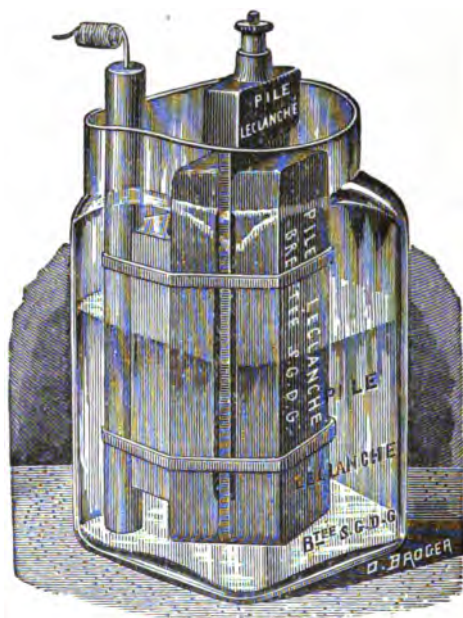
FIG. 100.—LECLANCHÉ CELL (GONDA FORM).

tightly as to preclude all possibility of danger to the connecting clamp from the creeping of salts or the escape of ammoniacal fumes. Attached to the carbon elements and held in position by soft rubber bands are two prisms or cakes, called "gondas," composed of a depolarizing compound similar to that already mentioned.

A still later form of cell, represented in Fig. 101, omits the carbon plate altogether and employs the agglomerate in the form of a hollow cylinder, within which the zinc rod is placed. This construction is known as the " Leclanché-Barbier system."

Another arrangement of the Leclanché-Barbier cell, repre-
sented in Figs. 102 and 103, has, besides the cylindrical mass

FIG. 101.—LECLANCHÉ-BARBIER CELL.

of agglomerate and the central zinc rod, a second zinc plate in
circular form outside of the agglomerate cylinder.   Fig. 102
shows the zinc rod provided with its wooden stopper which
closes the top of the agglomerate cylinder, and terminating
below in a small insulating tube of India rubber.

Another disposition of the Leclanché cell has been devised
by E. A. Wildt (1887).   The outer vessel is of ordinary
moulded earthenware and has three projections, one at the
centre of the bottom and one at each side near the upper
edge.

These projections serve to hold a curved glass partition pierced with conical holes. In the space limited by this parti-

FIG. 102.   LECLANCHÉ-BARBIER CELL.   FIG. 103.

tion is placed a carbon rod surrounded with crushed carbon and manganese binoxide, the upper part of which compartment is closed in order to prevent evaporation and to hold the rod in central position.

Bender and Francken (1886) have proposed the following agglomerate for the Leclanché cell:

Manganese peroxide .... 40 parts.
Graphite............................. 44   "
Tar.... 9   "
Sulphur.............................. 0.6   "
Water................................0.4   "

These substances are reduced to fine powder, mixed, moulded in metallic forms, then compressed, and finally, after desiccation, gradually heated to 350°.

Leclanché Cell with Immobilized Liquid.—The liquid of the Leclanché cell is rendered immovable in order to allow of the cell being more easily transported. Desruelles does this by placing in the cell filaments of asbestos or glass-wool dipped in solution of ammonium chloride, and Guérin by using a hot solution of *agar-agar*, a sort of sea-weed, found in oriental countries, which on cooling becomes a solid and elastic jelly.

Leclanché-Barbier Dry Pile.—The composition of this pile is not made public. It contains, however, a substance which is intended to absorb the solution of ammonium chloride.

Tyer Cell.—Glass vessel divided vertically into two compartments by a perforated plate of porcelain. In one compartment is placed the zinc, and in the other a piece of carbon surrounded with a mixture of manganese peroxide and crushed carbon. The cell is filled with a solution of ammonium chloride.

Clark and Muirhead Cell (1876).—Zinc contained in a perforated porcelain vessel surrounded with crushed carbon previously platinized and peroxide of manganese, platinized carbon, solution of ammonium chloride.

Howell Cell. (1879).—An exterior vessel of earthenware in which is placed another vessel of the same kind perforated laterally. Within the latter vessel is introduced a porous cup containing the zinc and a solution of ammonium sulphate in which is poured a few drops of mercury. A mixture of manganese peroxide and crushed carbon, together with the carbon electrode, fills the space between the exterior vessel and the perforated vessel. The whole is moistened with dilute sulphuric acid to which is added a small quantity of manganese sulphate. E. M. F. = 1.6 volts.

Leuchs Cell.—Zinc, 15 per cent solution of caustic potash ; porous cup, binoxide of manganese, carbon. E. M. F. = 1.9 volts.

Gaiffe Cell No. 1 (1875).—Zinc, solution of ammonium chloride; porous cup containing a carbon around which are alternate layers, superposed, of binoxide of manganese and granular carbon, as shown in Fig. 104. E. M. F. = 1.45 volts.

Gaiffe Cell No. 2 (1878).—Zinc, solution of zinc chloride ; hollow cylinder of carbon (Fig. 105) serving the double purpose of porous cup and electrode, in which are placed superposed layers of granular manganese binoxide and carbon.

Payerne Cell (1853).—Zinc, acidulated water ; porous cup, mixture of manganese peroxide and sulphuric acid. According to Payerne, this mixture, which does not disengage oxygen

at ordinary temperature, absorbs very readily hydrogen due to
the action of the zinc on the acidulated water.   According to
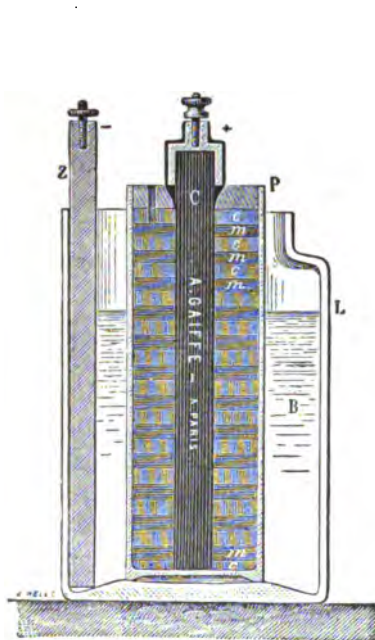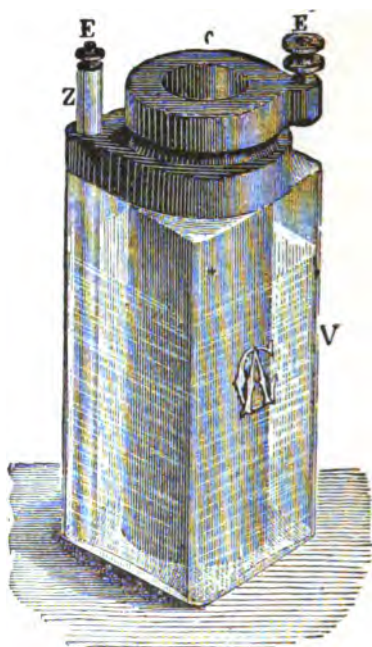
Le Roux, in order that the mixture of peroxide of manganese
and sulphuric acid may become efficient, it should be heated
to between 70° and 80° C.

  The A. X. O. Cell.—Carbon, sal-ammoniac, peroxide of
manganese and zinc are used in this cell as in the ordinary
Leclanché, the modifications and improvements consisting in
the employment of a carbon that, instead of being oblong, is
conical or pyramidal in shape, its sides inclining outward toward
the bottom and forming inclined planes, against which the
particles of the surrounding mixture press constantly by their
own weight. A contact by gravity is thus secured, which,
being automatic, is maintained at all times. Deep grooves
are moulded in the carbon, extending nearly the entire length

of the plate, and form a channel through which the bubbles of gas can escape.

Restoring Leclanché Cells.—Maîche has proposed to "regenerate" the Leclanché cell by submitting the exhausted element to a reverse current from a dynamo. The electrolysis of the zinc salts formed brings the manganese sesquioxide back to the state of peroxide, while zinc is precipitated on the zinc rod. Alliot has practically tested this, using a battery of eight cells, which he occasionally employed for lighting a couple of small glow-lamps for a few minutes at a time. By sending the current from a small dynamo through the cells once a week, for only a few minutes at a time, it was found that the Leclanches did not tend to polarize when feeding the lamps nearly as quickly as before. It will, however, scarcely be admitted that the zinc has been "regenerated" by this process, although, no doubt, the depolarizing effect of the reverse current results in restoring the cells to the most favorable condition for working, and where a current of sufficient E. M. F. is already available the hint may sometimes be worth taking.

(c) Oxide of Copper.

Denys Cell (1870).—Zinc^{Hg}, salt or acidulated water; porous cup, dilute sulphuric acid, cupric oxide, copper. This cell has been proposed as a substitute for the Daniell cell, over which, according to its inventor, it has the following advantages: very little sulphate of copper is formed at the time, and there is no direct reduction other than that which results from the action of the current; there is no formation of reduced copper in the pores of the porous cup, and the surface of the zinc remains always clean.

F. de Lalande and G. Chaperon Cell (1881).—Zinc^{Hg}-copper or iron surrounded with cupric oxide, 30 per cent solution of caustic potash. E. M. F. = 0.98 volt. With polar surfaces of 1 decimeter square, spaced 5 centimeters apart, the resistance equals 0.25 ohm. There are a number of forms of this cell, some of which are illustrated in Figs. 105, 106, 107, and 108.

In Fig. 106, *A* is a box of sheet-iron which serves to con-

tain solid potash when the cell is being transported, and cupric oxide when the cell is set up for work. The copper oxide is represented at *B*. *C* is the conducting wire of copper insulated with a rubber covering within the cell and connected to the box *A*. *D* is a spiral of amalgamated zinc which is supported on the cover *E*, and the upper end of this forms a terminal. The outer vessel *V* is of glass. The box *A* serves as the negative electrode.

In the construction shown in Figs. 107 and 108, the exterior vessel *V* is of iron, and therefore forms the negative electrode.

FIG. 106.—LALANDE AND CHAPERON CELL.

In Fig. 107, *G* is a cover of ebonite, which supports the zinc, *D*, which is in the form of a spiral and is supported by a
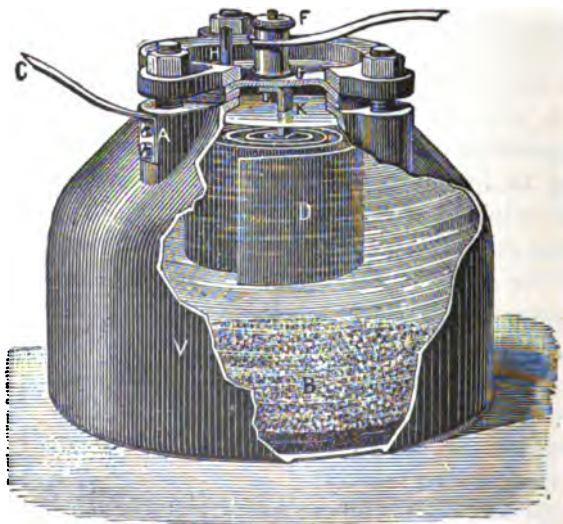
FIG. 107.—LALANDE AND CHAPERON CELL.

plate, K, of amalgamated brass. At F and C are the terminals of the cell, and at B the copper oxide.

In the form shown in Fig. 107, the outer vessel is of cast-iron and is shaped something like an elongated projectile. The copper oxide, B, is placed at the bottom of this, and the zinc, D, is in the form of a cylinder supported by the amalgamated brass rod K, which enters a rubber stopper in which is arranged a valve, H. The conducting terminal, C, is connected to the projection A of the vessel V. The other terminal is shown at F.
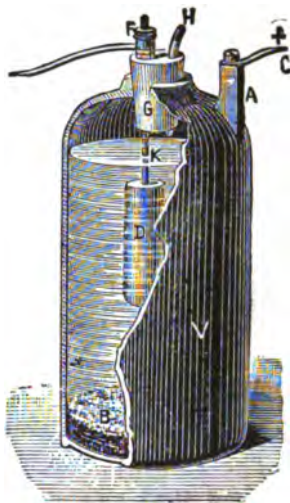
FIG. 108.—LALANDE AND CHAPERON CELL.

In the form shown in Fig. 109, A is a trough of iron, the bottom of which is covered with a layer of copper oxide, B. C is one terminal fastened against a plate of copper carried in the trough. The amalgamated zinc, D, is in the form of a plate, which is carried by an insulating support, L. M is the terminal connected to the zinc. In this form of cell, in order
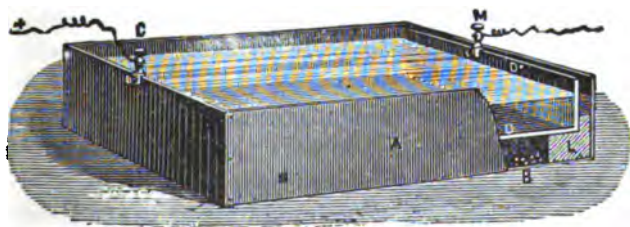
FIG. 109.—LALANDE AND CHAPERON CELL.

to hinder the carburization of the potash, the surface of the cell is covered with heavy petroleum oil. The Lalande and Chaperon cell has the advantage of not consuming the substances which it contains except in proportion to its work. The zinc and the copper oxide are not attacked by the alkaline solution. When circuit is closed, the water is decomposed,

and the oxygen, going to the zinc, produces zinc oxide, which combines with the potash to form alkaline zincate, while the hydrogen reduces the copper oxide to the metallic state.

This is represented by the following equations:

1. $Zn + 2H_2O = Zn(OH)_2 + H_2$.

2. $\begin{cases} Zn(OH)_2 = 2KHO = Zn(OK)_2 + 2H_2O; \\ H_2 + CuO = H_2O + Cu. \end{cases}$
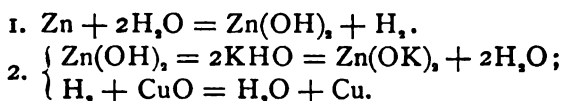
The thermic reaction is as follows: the oxidation of the zinc disengages 83.6 cal.; the combination of this oxide with the potash disengages about 8 cal. On the other hand, the decomposition of the copper oxide absorbs 40.4 cal. We have therefore, for the heat disengaged in this element,

$$C = (83.6 \text{ cal.} + 8 \text{ cal.}) - 40.4 \text{ cal.} = 51.2 \text{ cal.}$$

Applying the formula $E = \dfrac{C}{46.3}$ or $E = 0.0431 \times C$, we obtain a value equal to 1.10 volts.

The E. M. F. measured directly is, as is apparent, a little less than that indicated by theory. This is probably due to the fact that the heat of solution of the zinc oxide in potash has not been measured directly, but deduced from theoretical considerations.

By treating an exhausted cell as an accumulator, that is to say, by passing through it a reversed current, the various substances therein are brought back to their original condition; the copper integrally absorbs oxygen, and the alkali becomes regenerated while zinc is deposited; but the spongy state of the deposited zinc makes it necessary to submit it to new treatment or to receive it on a mercury support.

The Edison-Lalande Cell is a modification of the Lalande and Chaperon cell. It is represented in Figs. 110, 111, 112. *A* and *B* are two plates formed by mixing the copper oxide with 5 to 10 per cent of magnesium chloride, then moulding the same, and then exposing the same to a red heat until the mass is locked together. These plates are held by a channelled metal frame of copper, composed of a bottom piece, *a*, and two side pieces, pivoted to the bottom piece. To secure the oxide plates in

this frame the side pieces are swung open, and the oxide plates are slipped down between them. The side pieces are then closed on the oxide plates and are secured by a copper band. The top of the glass jar is closed by a cover, D, made, preferably, of porcelain and having openings through which the upper ends of the side pieces project. A connecting wire is secured to one of the projecting ends of the side pieces. The cover, D, is moulded with a central rib, f, extending transversely part way across it. Two zinc plates, $E\,E'$, are supported from the under side of the cover D, on opposite sides of the rib f. Metal pins, g, from the zinc plates pass upward through the cover D, and enter a metal block, F, in which they are secured by set-screws, h. Between the

Fig. 109.—Edison Lalande Cell.

two zinc plates is located the negative electrode formed of the copper oxide plates, A, B, and the sustaining frame. The solution employed is preferably a 25 per cent solution of caustic soda or caustic potash. The caustic soda solution is made by filling the outer vessel with water and inserting sticks, G, of caustic soda, which dissolve slowly, without producing the heat which would be caused if the powdered material were put directly into the water. Two other forms of Edison-Lalande Cell are represented in Figs. 111 and 112.
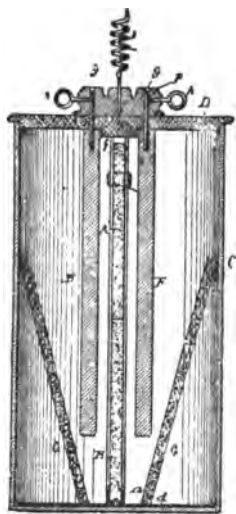
The weight of the oxide plate for a 15-ampere-hour cell is about 56 grams; for a 300-ampere-hour cell about 1 kilogram. A layer of heavy paraffin oil is placed above the solution of caustic soda or potash to prevent formation of carbonate, due to exposure of the liquid to the air. This is of importance, since without the oil the lifetime of the cell is greatly reduced. A 300-ampere-hour cell measures 11.25 inches in height by $5\frac{3}{8}$ inches in diameter. E. M. F. = about 0.7 volt; internal resistance about 0.03 ohm. On open circuit there is scarcely any local action.

(d) Lead Oxide.

Morgan Cell (1881).—Zinc, solution of ammonium chloride, litharge, lead. The litharge is placed in the bottom of the jar and surrounds the lower part of the lead electrode. The chemical reaction consists in the formation of double chloride
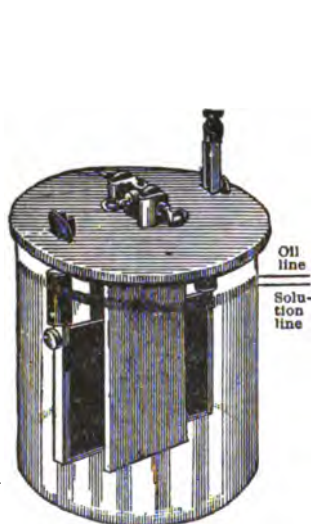
FIG. 111.
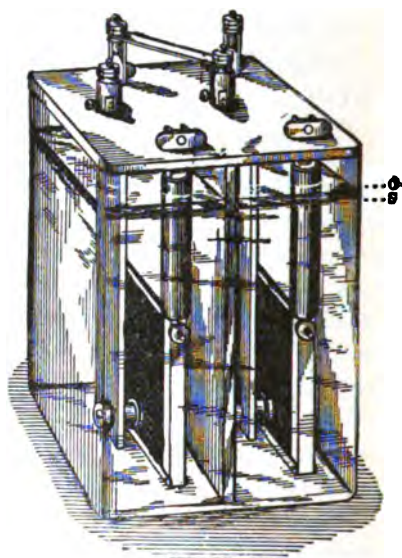
FIG. 112.

EDISON-LALANDE CELLS.

of ammonium and zinc, disengagement of ammoniacal gas, and reduction of the lead oxide to the metallic state.

Gaiffe Cell (1872).—Zinc, solution of ammonium chloride; minium (Pb_3O_4), lead. E. M. F. = 0.5 to 0.6 volt. The minium occupies the bottom of the jar and surrounds the lower part of the lead electrode. This cell works only in closed circuit.

(e) Ferric Oxide.

Clamond Cell (1874).—Zinc, solution of ammonium chloride; porous cup containing ferric oxide (Fe_2O_3), obtained by precipitation, and fragments of coke, the whole packed around a carbon electrode.

Brémond Cell (1884).—In a porous cup is placed a carbon

cylinder surrounded with a mixture of ferric oxide and pow-
dered carbon, the whole enveloped in a serrated network of
iron wire.   The cell thus constituted is placed in a cesspool or
sewer.   The iron network is the positive electrode.   The
alleged chemical reaction (doubtful) is the formation of iron
sulphide and reduction of the ferric oxide.

(f) Sulphates of Mercury.

Marié-Davy Cell (1859).—Zinc, water pure or acidulated ;
porous cup containing a thick paste of sulphate of mercury in
which the carbon electrode is placed.   E. M. F. = 1.3 to 1.5
volts.   The paste is prepared by soaking the pulverized salt in
water.   Mercuric sulphate (SO_4Hg), mercurous sulphate
(SO_4Hg_2), or turbith mineral (SO_4Hg_3) may be used in this
cell without sensibly varying the E. M. F.   Turbith mineral
is a yellow compound produced when mercuric sulphate is
soaked in water according to the equation

$$3SO_4Hg + (n + 2)H_2O = SO_4Hg_3 + 2SO_4H_2 + nH_2O.$$

The basic salt (turbith mineral)
is partly decomposed and a portion
remains in solution in the acid liquor.
According to Ditte, water containing
sulphuric acid acts in the same way
so long as the acid does not exceed
82 grams to the litre.   Fig. 113 repre-
sents a Marié-Davy battery of two
elements.   For telegraph service mer-
curous sulphate is exclusively used in
this cell on account of its long life-
time.   The following shows the in-
fluence of temperature on the Marié-
Davy cell (Sabine) :
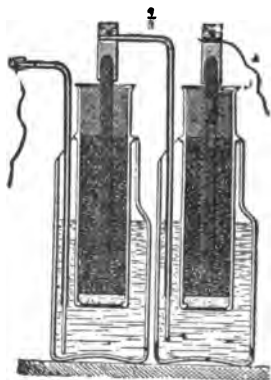
Fig. 113.—MARÉI-DAVY BATTERY.

Temp.	E. M. F.
21° C........................	1.412 volts.
21° " after 3 hours...............	1.339 "
22° " " 24 "	1.412 "
100° "......	1.322 "

Menna Apparicio Cell.—Glass vessel in the bottom of which is a carbon disk surrounded with a paste of mercuric sulphate. Above this paste is a layer of fine sand, and above the sand a disk of zinc. The cell is filled with ordinary water.

Grenet Cell (1863).—Zinc-carbon, mercurous sulphate. The sulphate is at the bottom of a receptacle filled with pure water. The carbon is immersed in the mercurous sulphate, and the zinc enters the water without touching the sulphate.

Gaugain Cell.—Zinc, carbon, mercuric sulphate. Same arrangement as in the Grenet cell.

Trouvé Reversing Cell.—This cell, shown in Fig. 114, con-
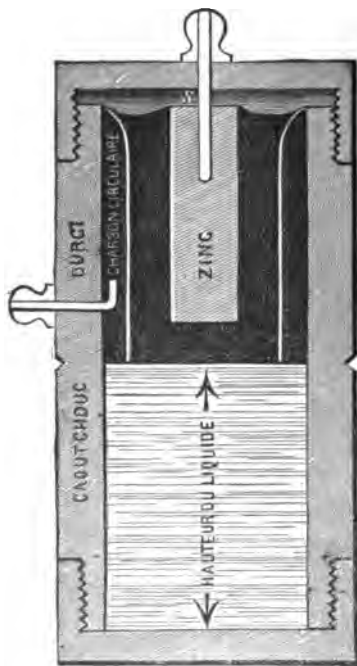
FIG. 114.—TROUVÉ REVERSING CELL.

sists of a zinc and a carbon contained in an hermetically sealed case of ebonite. The electrodes occupy the upper half of the

case, the lower half being filled with a mixture of sulphate of mercury and water which forms the exciting liquid. As long as the case is held vertically the electrodes do not enter the liquid, but as soon as the cell is turned the liquid flows upon the electrodes and the action begins.

Beaufils Cell (1881).— Zinc, acidulated water; agglomerate of mercuric sulphate, powdered carbon, and paraffine combined hot. E. M. F. = 1.5 volts.

Chardin Cell.—Zinc, car-

FIG. 115.—CHARDIN BATTERY.

bon, solution of mercuric sulphate containing an excess of sulphate. E. M. F. = 1.526 volts. Fig. 115 shows a battery of these cells. The electrodes are attached to a plate, *A*, which normally occupies the empty jars on the right, but which is placed in the vessels containing the mercuric sulphate when the battery is to operate. As the lid of the containing case cannot be closed so long as the electrodes are in the last-named position, this serves as a reminder to the operator to replace the electrodes in the empty jars and so stop the action of the battery when it is no longer needed.
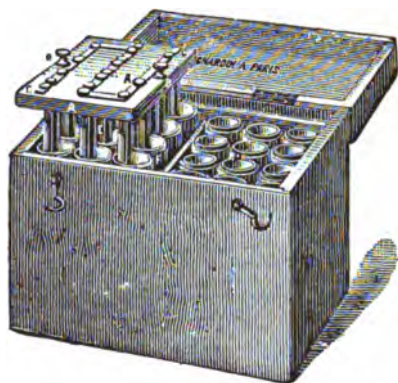
M. Chardin has also devised a sort of floating electrode cell which is represented in Fig. 116. Each element consists of a glass test-tube, *V*, containing two floats of paraffined cork, mercuric sulphate, and water. When the cell is charged and at rest, the disposition is such that the electrodes *Z* and *C* rest upon the floats *L*, which are of course in the upper part of the containing jar. When the plate *M* is

FIG. 116.—CHARDIN CELL.

placed on the electrodes so as to push down the floats, or when the test-tube is elevated, the electrodes enter the liquid.

Latimer Clark Standard Cell (Fig. 117).—A cell is formed by employing pure mercury as the negative electrode, the mercury being covered with a paste formed of mercurous sulphate in a thoroughly saturated solution of zinc sulphate; the positive electrode consists of pure distilled zinc resting on the paste.
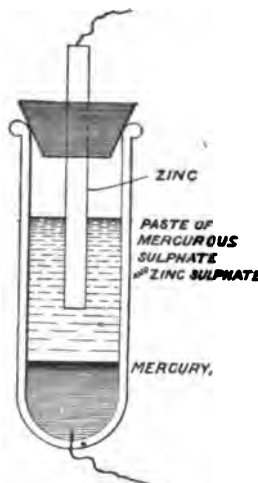
FIG. 117.—LATIMER CLARK STANDARD CELL.

The best method of forming the paste is, according to Lord Rayleigh, as follows: Rub up in a mortar 150 grams of mercurous sulphate, 5 grams of zinc carbonate, and use sufficient zinc sulphate solution (not *super*saturated) to make a thick paste. Leave the whole in the mortar for two or three days, occasionally pounding it up in order to allow the carbonic anhydride which forms to escape. Dr. A. Muirhead, who has had a very lengthened experience with the Clark cells, prefers to make the paste as follows:

A saturated solution of zinc and mercurous sulphate is prepared by heating in the saturated solution of zinc sulphate a portion of the mercurous sulphate, adding thereto a little free mercury to preserve the basicity of the mercurous salt; mercurous sulphate is then mixed into a paste with the solution so prepared. The mercurous sulphate can be obtained commercially; but it may be prepared by dissolving pure mercury in excess in hot sulphuric acid, at a temperature below boiling point. The salt, which is a nearly insoluble white powder, should be well washed in distilled water, and care should be taken to obtain it free from the mercuric sulphate (persulphate), the presence of which may be known by the mixture turning yellowish on the addition of water. The careful washing of the salt (according to Clark) is a matter of essential

importance, as the presence of any free acid, or of persulphate, produces an irregularity in the electromotive force of the cell for some time after charging. The paste is poured on to the surface of the mercury (which should have been distilled in vacuo); a piece of pure zinc is then suspended in the paste, and the vessel sealed up with marine glue (*not* paraffin wax). Contact with the mercury may be made by means of a platinum wire passing down a glass tube, cemented to the inside of the cell, and dipping below the surface of the mercury, or more conveniently by a small external glass tube blown on to the cell and opening into it close to the bottom.

Muirhead Improved Clark Standard Cell.—The usual forms of the Clark cell, especially when newly set up, are unsuitable for transport; the mercury, being free, is apt to leave the platinum wire contact when the cell is inverted or upset, and to fall through the paste into contact with the zinc rod, thereby either short-circuiting the cell altogether or destroying the value of its electromotive force. To remedy this defect Dr. A. Muirhead constructs the cell as shown by Fig. 118. *A* is a flat, closely-wound spiral of platinum wire (shown in plan in the lower part of figure) which has been coated or amalgamated with pure mercury, either by boiling it in the latter or by dipping the spiral, when heated red hot, into mercury; the continuation of the wire is sealed into the glass cell, forming the outer connection. *Zn* is a rod of pure zinc supported by a

FIG. 118.—MUIRHEAD STANDARD CELL.

cork, and imbedded in the cement stopper *c*. Inside the cell is placed a paste, *p*, composed of pure mercurous sulphate and a saturated solution of pure zinc sulphate.

The electromotive force of the two Clark cells is, according

to Lord Rayleigh, 1.454 B. A. volts at 15° C. The effect of change of temperature of $t°$ C. is

$$E = 1.454 \{1 - .00077 (t° - 15)\} \text{ volts.}$$

The following table shows the electromotive force at various temperatures calculated from the foregoing formula :

TABLE SHOWING E. M. F. OF CLARK STANDARD CELL AT VARIOUS TEMPERATURES. (KEMPE.)

Temp. Deg. C.	B. A. Volts.	Temp. Deg. C.	B. A. Volts.	Temp. Deg. C.	B. A. Volts.
0	1.471	11	1.458	22	1.446
1	1.470	12	1.457	23	1.445
2	1.469	13	1.456	24	1.444
3	1.467	14	1.455	25	1.443
4	1.466	15	1.454	26	1.442
5	1.465	16	1.453	27	1.441
6	1.464	17	1.452	28	1.439
7	1.463	18	1.451	29	1.438
8	1.462	19	1.450	30	1.437
9	1.461	20	1.448	31	1.436
10	1.460	21	1.447	32	1.435

Subsequent investigations by Lord Rayleigh place the E. M. F. of the Clark cell (Rayleigh pattern) at 1.435 true volts, equal to 1.455 B. A. volts at 15° C. The preceding equation would therefore read :

$$E = 1.435 \{1 - .00077(t° - 15)\} \text{ volts.}$$

In order that the force in the Clark cells may preserve its value constant, care must be taken that the cells are not worked through a low resistance. It is necessary, therefore, in employing them, to see to it that they are only used in circuits of a very high resistance, or for charging a condenser, or are balanced by a secondary battery.

Carhart-Clark Standard Cell.—The novel constructive feature in this form of the Clark cell (devised by Professor H. G. Carhart) is the introduction of an extra graphite resistance of about 10,000 ohms resistance, the object of which is to prevent

injury to the cells should it become accidentally short-circuited
for a brief period. The employment of pure chemicals and
careful handiwork is claimed to result in a reduction of the
temperature coefficient to about .03 of one per cent per degree
centigrade.

In all standard cells where a correction for variation in
E. M. F. due to temperature changes is necessary, the use of a
thermometer for determining accurately the temperature is
implied, so that, strictly speaking, the term "standard" is not
properly used, for no instrument is absolutely standard which
depends upon the accuracy of some other instrument. As·
thermometers are as a class by no means exact measuring ap-
paratus—their indications depending, for example, upon slight
changes in diameter of the mercury tube and other variations
of a mechanical or physical nature—plainly it follows that, for
exact work, the thermometer error, in addition to the tempera-
ture coefficient of the cell, must be known for every particular
case. A certain cell, therefore, in which both factors are
accurately determined may *per se* be standard, but this is not
necessarily true of a cell of which only the E. M. F. at certain
temperatures is known, when there is an uncertainty in the
temperature measurement.

The desideratum is, of course, a cell which, by reason of the
physical and chemical properties of the substances in it, shall
practically not vary at all in electromotive force within ordinary
temperature ranges; and this, according to Mr. Edward Wes-
ton, has been accomplished.

Edward Weston Standard Cell.—Mr. Edward Weston·
claims the remarkable and important discovery of a standard
cell the electromotive force of which is practically independent
of temperature changes; in other words, one in which the
chemical affinities are substantially the same, no matter what
the temperature of the cell may be, within reasonable limits;
thus realizing the unusual condition of the action of chemical
affinities being practically unhelped by heat. The special cell
in which his discovery is embodied, and which, out of the many
forms tested, has so far given the best results, contains as an

electrolyte a cadmium salt in solution, and one cadmium elec-
trode. Any salt of cadmium may be used, the acid of which
forms a practically insoluble compound with mercury when
the salt is in the state of a saturated solution in water, or in a
solution of the salt of cadmium employed. Such salts, for
example, are the sulphate, the chloride, the bromide and the
iodide. These salts are equally as soluble in cold as in hot
water, and the density of the solution despite temperature
changes remains the same.

With a cell composed of electrodes respectively of an
amalgam of cadmium and mercury and of pure mercury and
sulphate of mercury with a saturated solution of a cadmium
salt as an electrolyte, it is found that there is, first, no variation
of electromotive force due to changes of temperature ; second,
no disturbing currents due to local action ; third, no potential
differences due to greater or less density of solution as affect-
ing one electrode or the other, or to differences of temperature
of one electrode or the other. The construction of the
Weston cell is represented in Fig. 119.

A is an outer shell or casing made preferably of sheet brass
and elliptical in form. In the bottom of this shell is inserted
a wooden block, *B*, containing cavities or recesses to receive
the glass cell *C C'*. The said glass cell consists of two cylin-
drical vessels, *C C'*, connected by a transverse tube, *D*. The
lower ends of the said vessels are rounded and their mouths
are flared, as shown. Within one vessel, as *C*, is an amalgam
of cadmium and mercury. In the other vessel is a mixture of
pure mercury and protosulphate of mercury. In each vessel,
above the electrode, is placed a piece of cloth, *E*, the edges of
which turn upwards. In the cup-shaped piece of cloth thus
introduced is inserted a cork, *F*, pierced with apertures, *G*.
This arrangement of cork and muslin serves to hold the
materials of the electrodes in place and prevent their becom-
ing commingled with the solution when the cell is moved
about. At the same time, the openings in the corks *F* allow
of free contact of the solution with the electrodes. There is
then placed in each vessel, *C C'*, a saturated solution of cadmium

sulphate. Lastly, in the mouths of the vessels suitable stoppers, *M*, are inserted and secured in place with cement. The connecting wires *H* pass through the bottoms of the vessels *C C'* and communicate electrically with the electrodes. They are connected to copper wires, *I*, which are received in suitable binding posts, *J*. These binding posts *J* are carried by thecover, *K*, of the shell *A*, which cover is made of rubber. The bind-
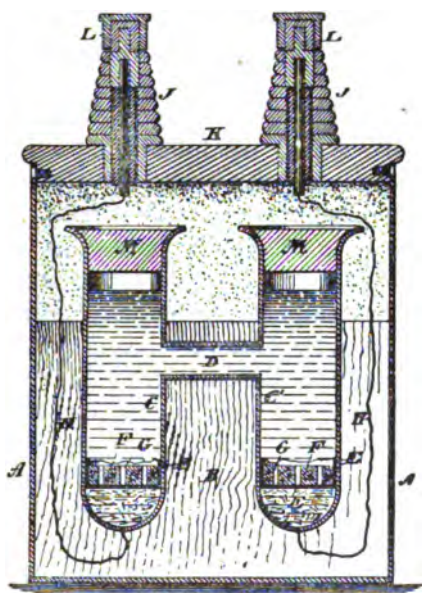
FIG. 119.—WESTON STANDARD CELL.

ing posts *J* are provided with covering caps, *L*, as shown. After the cell is in place, the space in the shell *A* above the block *B* is filled up with a composition preferably composed of beeswax, rosin, and linseed oil. The cover *K* is then adjusted and the cell permanently closed. The electromotive force of the cell described approximates 1.019 volts.

Gouy Standard Cell.—Oxide of mercury is used instead of the sulphate as a depolarizer, and instead of a saturated solution of zinc sulphate a ten per cent solution is employed.

E. M. F. = 1.39 volts at 12° C.   The temperature coefficient is claimed to be only 0.01 per cent per degree C.

Baille and Féry Standard Cell.—The negative electrode is powdered lead chloride, precipitated from a warm solution and in crystalline state.   It is held in an upwardly curved tube depending from the cover of the cell, and has a lead wire leading to the binding post embedded in it.   The positive electrode is Zinc^{Hg}, and the liquid a solution of zinc chloride of density 1.157.   With this solution E. M. F. = one half volt.   Temperature variation, according to Carhart, amounts to "only 0.005 volt in 46° C."

Observations of Du Moncel upon Sulphate of Mercury Cells.—*Du Moncel* (1873) has found that a solution of pure mercuric sulphate causes with a negative electrode of mercury only a hardly appreciable secondary current.   A few particles of sodium bicarbonate or zinc sulphate added to the solution results in the production of an energetic secondary current. Thus it occurs that sulphate of mercury cells which polarize but feebly when new, become very inconstant after moderate usage when the reduced mercury in contact with the carbon is in presence of a more or less concentrated solution of zinc sulphate or other impure salt, such as always exists in commercial sulphates of mercury.   For this reason, Du Moncel advises that the porous cups of such cells be made with a double perforated bottom in order to isolate the carbon from the mercury and from the liquid charged with zinc sulphate. (See Polarization.)

(g) Lead Sulphate.

Becquerel Cell (1846).—Zinc, solution of sodium chloride; porous cup, solution of sodium chloride holding lead sulphate in suspension, lead, carbon.   E. M. F. = 0.59 volt.   The chemical reactions are as follows:

1. $Zn + 2H_2O = Zn(OH)_2 + H_2.$
2. $H_2 + SO_4Pb = SO_4H_2 + Pb.$
3. $SO_4H_2 + Zn(OH)_2 = SO_4Zn + 2H_2O.$

The final reaction being
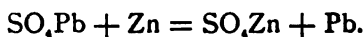
$$SO_4Pb + Zn = SO_4Zn + Pb.$$

The thermic reaction is as follows : The heat disengaged is equal to the heat of formation of zinc sulphate less the heat of decomposition of the lead sulphate; or, C = 107.0 cal. — 74.8 cal. = 32.2 cal.   Applying the formula $E = \dfrac{C}{46.3}$ or $E =$ 0.0431 + C, we have E. M. F =·0.69 volt, which is nearly that found by experiment.

E. Becquerel Cell (1860).—Zinc, solution of sodium chloride, carbon covered with a paste consisting of lead sulphate in fine powder 100 grams, sodium chloride 25, and saturated solution of sodium chloride 50 c. cm., which hardens as easily as plaster.

Marié-Davy Cell (1859).—Disk of tinned iron covered with a paste of lead sulphate mixed with pure water, either salt or containing zinc sulphate, upper disk of zinc.   The battery contains some forty couples arranged after the fashion of Volta's pile.   Another arrangement designed by the inventor for medical use consists of a disk of tinned iron, disk of zinc, and between these a disk of blotting-paper covered with zinc sulphate mixed with gum-water.

(h) Mercurous Chloride.

Heraud Cell (1879).—Zinc, solution of ammonium chloride ; canvas bag containing a paste of mercurous chloride (Cl_2Hg_2) and a carbon.   E. M. F. = 1.45 volts at the beginning; after six months' use E. M. F. = 1.075 volts.   Intermediate reactions aside, the action of the ammonium chloride on the zinc when the circuit is closed may be represented by the following equations :

$$2ClNH_4 + Zn = Cl_2Zn + H_2 + 2NH_3.$$
$$Hg_2Cl_2 + H_2 + 2NH_3 = 2ClNH_4 + 2Hg.$$
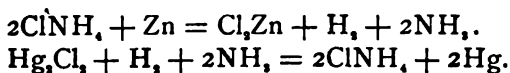
That is to say, there is produced ammonium chloride capable of maintaining the exciting liquid in its normal state of con-

centration and metallic mercury. There is also formed mer-
curous chloride with amide base (Cl_2Hg_2,$Hg_2(NH_2)_2$) and
ammoniacal oxychloride of zinc.

(i) Lead Chloride.

Marié Davy Cell.—A piece of thick unsized paper is painted
over on one side with a mixture of lead chloride and gum-
water. This paper is cut into disks, which are mounted in a
pile between disks of tinned iron and zinc.

Pierlot Cell.—Zinc[Hg] enclosed in a bag of parchment-paper;
lead chloride, pure water, lead.

(j) Silver Chloride.

Gaiffe Cell.—Zinc, silver surrounded with silver chloride,
5 per cent solution of zinc chloride. E. M. F.= 1.02 volts.
According to Du Moncel, when a solution of sodium chloride is
employed in the silver chloride cell, a small quantity of chlorine
is disengaged. This is not produced when a zinc chloride
solution is used. For medical uses M. Gaiffe arranges his cell
without liquid. The zinc and the silver wire covered with
silver chloride are simply separated by several layers of
blotting-paper moistened with a zinc chloride solution.

Skrivanow Cell.—Zinc, solution of 3 parts caustic potash
and 4 parts water ; bag of parchment-paper containing silver
chloride, silver. E. M. F. = 1.45 volts. A cell weighing 100
grams is said to yield 1 ampere-hour. A cell containing 700
grams of zinc and 2500 grams of silver chloride is said to be
able to furnish uninterruptedly for 20 hours, work equal to
180,000 kilogrammeters.

Warren de la Rue and Muller Cell (1868) (see Fig. 120).—
Zinc, silver wire covered with melted silver chloride, solution
of 25 grams of sodium chloride in 1 litre of distilled water.
E. M. F. = 0.97 volt. In order to avoid accidental contact
of the electrodes, a rod of silver chloride is placed in a small
hollow tube of parchment-paper, through two openings in the
upper part of which the silver wire passes. In later forms of

this cell an equal quantity of ammonium chloride replaces the silver chloride. E. M. F. = 1.03 volts. The resistance is from 3 to 4 ohms, increasing as oxychloride forms on the zinc, sometimes to 30 or 40 ohms (Sprague). The deposit can be removed by dipping in dilute HCl. When this cell is first used it is necessary to close the circuit for about 15 minutes, when
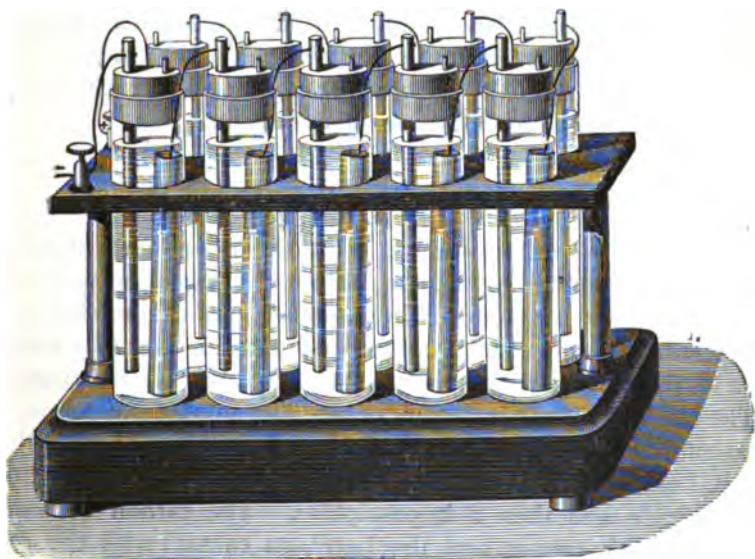
FIG. 120.—DE LA RUE AND MULLER BATTERY.

the cell attains its normal E. M. F. The final chemical reaction (neglecting intermediate reactions) is represented as follows:
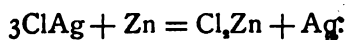
$$3ClAg + Zn = Cl_2Zn + Ag:$$

The thermic reaction is as follows: The heat disengaged is equal to the heat of formation of zinc chloride, less heat of decomposition of silver chloride; or,

$$C = 112.8 \text{ cal.} - (29.2 \text{ cal.} \times 2) = 54.4 \text{ cal.};$$

whence E. M. F. $= 0.0431 \times C = 1.17$ volts, which approximates closely that found by experiment. On substituting in this element for silver chloride, silver bromide or iodide the E. M. F. becomes 0.908 for BrAg and 0.758 volt for IAg. The cell is employed chiefly for testing purposes and for medical uses, and is of little utility except for the production of small currents.

A remarkable battery of some 15,000 of these cells was built at the Royal Institution, London, by Mr. De la Rue. His experiments are reported in the *Electrician*, Vol. IX, p. 77.

Pinkus Cell (1868).—Zinc, silver capsule filled with precipitated silver chloride, salt or acidulated water.

(k) Various Depolarizers (Compound Bodies).

Mauri Cell (1881).—Zinc, solution of sodium chloride; porous cup, containing a paste composed of equal parts of sulphur, cuprous sulphide (SCu_2), and of graphite mixed in a concentrated solution of sodium or potassium nitrate, carbon. E. M. F. $= 1.1$ volts (open circuit) and 0.95 volt (closed circuit). The alkaline nitrate is decomposed. The sulphide of copper is transformed into nitrate and sulphate of copper. The alkaline metal of the nitrate combines with the sulphur, producing first a sulphide and then a hyposulphite. The carbon becomes covered with copper, and the latter, on contact with the sulphur, is transformed into sulphide.

Ney Cell (1868).—Zinc[Hg], solution of ammonium chloride; porous cup, paste of copper carbonate, carbon. According to Ney, copper carbonate is insoluble in an ammonium chloride solution; but on closing the circuit the chloride is decomposed into hydrochloric acid and ammonia; the acid accumulating at the positive and the ammonia at the negative electrode. Afterwards the copper carbonate enters into solution in the ammonia, and produces a current of the force and constancy of that of the Daniell cell.

Fitzgerald and Molloy Cell.—A vessel divided into two compartments by a carbon plate, which serves both as diaphragm and as negative electrode. In one compartment is sulphuric

acid and a zinc plate, in the other a mixture of chromate of lime and concentrated sulphuric acid. Sulphate of chromium, sulphate of calcium, and oxygen are formed, which combine with the hydrogen resulting from the decomposition of the acidulated water by the zinc.

Skrivanow Cell.—Zinc, body of asbestos, saline paste, carbon. E. M. F. = 1.5 to 1.6 volts. The paste consists of ammoniacal chloride of mercury 100 parts, chloride of sodium 30, and chloride of silver 2.5 melted together. When the mass is covered, it is ground and made into a paste with a concentrated solution of zinc chloride.

Pérémé. Cell.—Zinc, pure water; porous cup, paste of antimony sulphate, carbon. E. M. F. = 0.6 volt (about).

Fechner Cell (1831).—Zinc, copper, acidulated water or ammonium chloride solution. The face of the copper on the zinc side is coated with copper sulphide by the application of a potassium sulphide solution. When the circuit is closed, the disengaged hydrogen reduces the copper sulphide to an adherent rough deposit of metallic copper.

CHAPTER X.

CELLS HAVING TWO LIQUIDS. (*Continued.*)

I. CELLS HAVING DIFFERENT ELECTRODES. (*Continued.*)

(3) DEPOLARIZATION BY THE DEVELOPMENT OR APPLICATION OF ELEMENTARY BODIES.

(a) Chlorine.

Le Roux Cell (1853).—Zinc, acidulated water; porous cup mixture of peroxide of manganese and hydrochloric acid, carbon. The hydrochloric acid on contact with the peroxide disengages chlorine, which combines with the hydrogen from the decomposition of the acidulated water by the zinc. The production of chlorine takes place according to the following equation:

$$MNO_2 + 4HCl = 2H_2O + Cl_2Mn + Cl_2.$$
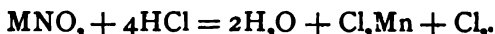
D'Arsonval Cell.—Zinc, ordinary water; porous cup filled with crushed retort-carbon surrounding a carbon electrode. The depolarizer consists of 1 vol. of water saturated cold with potassium bichromate and 1 vol. of ordinary hydrochloric acid. The liquid should escape continuously. The cell is odorless, E. M. F. = 2 volts. The chemical reactions are as follows:

1. $Cr_2O_7K_2 + 2HCl = 2ClK + H_2O + 2CrO_3.$
2. $2CrO_3 + 12HCl = Cr_2Cl_6 + 6H_2O + 6Cl.$

The chlorine combines with the hydrogen disengaged by the zinc.

Upward Cell (1886).—*A*, Figs. 121 and 122, is a glazed

earthen vessel containing a porous jar. Inside the porous jar is placed a slab of zinc. Carbon plates, *C C*, are placed on each side of the porous jar, and surrounded by granular crushed carbon packed and pressed closely together. The top of the carbon compartment of the cell is hermetically sealed. The zinc plate, *Z*, in this jar is surrounded by a solution of chloride of zinc. When the cell is required for use, gaseous chlorine enters, or rather is drawn into, the cell at *D*. A lead pipe, *E*,
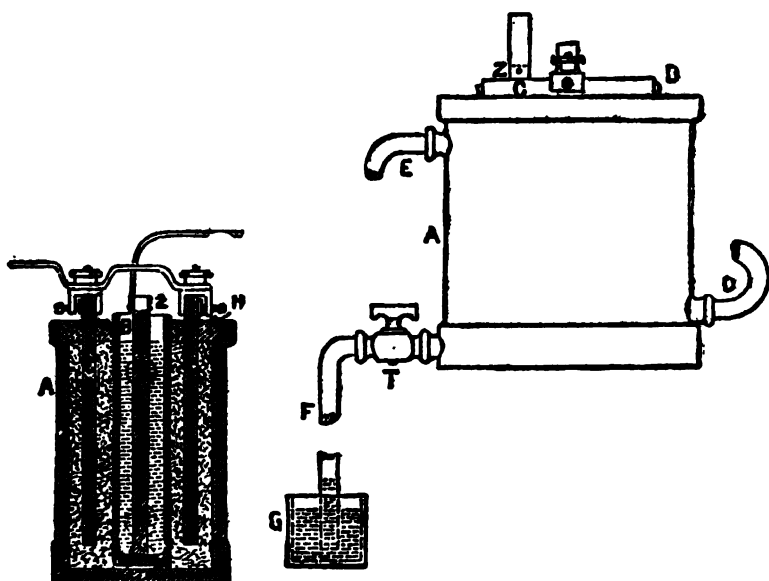
FIG. 121.   UPWARD CELL.   FIG. 122.

goes from the top of one cell to the bottom of the next, and the gas passes from cell to cell through these pipes.

The zinc chloride solution which is formed by the working of the battery very slowly percolates through the porous pot, *B*, into the outer cell, and insures the broken carbon remaining moist; but the tap, *T*, which is always open, prevents any liquid accumulating in the outer cell; allowing it to run down through the pipe *F* into the trough below. The level of the liquid in this is always kept above the orifice of the tubes,

so that no gas escapes, while an overflow is provided into the house-drain. (ZnCl, is an excellent disinfectant.) The gas arrives from the holders, and passes into a bubbling bottle, from which it enters the lower part of the first cell ; the exit at the upper part of this cell is connected by a tube to the inlet at the lower part of the second cell, and so on through all the cells in series ; the exit of the last cell being connected by a tube, through another bubbling bottle, to a simple water aspirator or ejector.

Assuming the cells to be all full of gas and the circuit closed, the gas will be equally consumed in every cell in proportion to the current ; and, as the carbon cells are hermetically sealed, a vacuum is gradually produced, thus drawing further supplies of gas from the holder. If the chlorine were absolutely pure, no further feeding would ever be required, as the cells would always keep themselves supplied from the holder.

In practice, however, it is not possible to prevent the admixture of a small quantity of air (say 3 per cent), and a consideration of the conditions will show that this air must first accumulate in the last cell.

The E. M. F. of this last or right-hand cell will, therefore, drop before that of the others is in the slightest degree affected, and this drop is arranged to open automatically the aspirator and to cause the removal of the accumulated air.

The E. M. F. claimed is 2.1 volts. It is further asserted
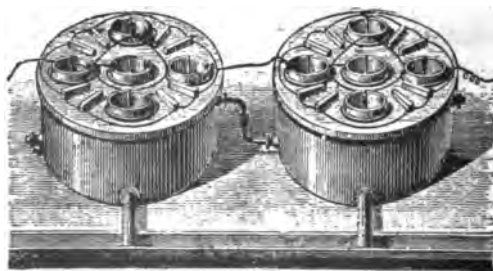
FIG. 123.—UPWARD BATTERY.

that, inasmuch as the whole of the chemical changes are the combustion of zinc or iron by chlorine and that purely electro-

lytically, there is no local action. A modified form of this cell is represented in Fig. 123, in which gas entering the apparatus drives the air before it. Each element comprises eight carbon plates connected for quantity, and five cleft cylinders of zinc placed in porous vessels and connected with each other.

(b) Bromine.

Koosen Cell (1884).—Platinum, bromine ; porous cup, acidulated water, zinc^{Hg}. E. M. F. = 1.9 volts, which remains the same when carbon is substituted for the platinum. The platinum plate is corrugated or wavy in shape. The porous cup contains a body of mercury.

(c) Iodine.

Doat Cell (1856).—Mercury, solution of potassium iodide ; plate of porous porcelain on which are placed pieces of retort-carbon and iodine crystals. The cell has a rectangular cup-shape. E. M. F. = o. 6 volt. The terminals connect with the mercury and the carbon respectively. The chemical reactions are as follows : 1. The potassium iodide decomposes on contact with the mercury, producing mercurous iodide, which is rapidly transformed into mercuric iodide. 2. The potash which is set free combines with the iodine and re-forms potassium iodide. 3. The mercuric iodide partly dissolves in the potassium iodide (double iodide of mercury and potassium), but this solution, instead of diminishing the attack of the mercury (as sulphate of zinc does in ordinary cells), on the contrary favors it, and thus renders the current constant. Regnauld has studied various cells based on the Doat cell, and finds the following E. M. F's :

	Iodine and Iodide.	Bromine and Bromide.	Chlorine and Chloride.
Mercury................	0.6 volts.	0.96 volts.	1.07 volts.
Zinc	1.19 "	1.63 "	1.98 "
Sodium amalgam........	2.04 "	2.47 "	2.97 "
Potassium amalgam.....	2.05 "	2.54 "	3.08 "

(d) Oxygen.

In all cells having a single non-depolarizing electrolyte the oxygen of the air acts as the depolarizing substance. Among these the best are those of the Smee and Maîche types.

In cells having two liquids in which an ox-acid (nitric acid, for instance) or an oxy-salt (such as copper sulphate) acts as depolarizer, the oxygen contained in these compounds in reality does the work.

(e) Sulphur.

Matteucci Cell (1865).—Zinc, sodium chloride solution; porous cup, flowers of sulphur, salt water, lead.

Blanc Cell (1865).—Zinc, copper, solution of sodium chloride to which flowers of sulphur is added.   E. M. F. = 0.6 to 0.4 volt.   The copper electrode, which extends to the bottom of the vessel, should be covered with an insulating layer at its upper portion and a layer of sulphide of copper at its lower portion.   A quantity of flowers of sulphur is packed around the lower part of this electrode; the plate of zinc is immersed about half way.   The hydrogen here combines with the sulphur and forms hydrosulphuric acid, which decomposes the sodium chloride, producing sodium sulphide and hydrochloric acid; the latter then attacks the zinc and transforms it into chloride, which in its turn is converted into zinc sulphide by the sodium sulphide which at the same time is formed from the sodium chloride.

Savary Cell (1868).—Zinc, solution of sodium chloride; porous cup, paste of sulphur, with salt water, carbon surrounded with a spiral copper wire.   E. M. F. = about 1 volt.

De Laurier Cell (1870).—Iron vessel containing a paste of slaked lime, flowers of sulphur, and sodium chloride with water. In the middle is a zinc cylinder the lower end of which rests on an insulating body which prevents contact with the iron. Double chloride of zinc and sodium, zincate of sodium and calcium sulphide, are produced.

CHAPTER XI.

CELLS HAVING TWO LIQUIDS. *(Continued.)*

II. CELLS HAVING IDENTICAL ELECTRODES.

(1) CELLS HAVING LIQUID DEPOLARIZERS.

Becquerel Oxygenated Gas Cell (1838).—Platinum, potash solution; porous partition, nitric acid, platinum. When the circuit is closed, bubbles of oxygen gas appear around the electrode immersed in the potash. The water of the potash solution is decomposed, oxygen is freed on the platinum plate, and the nascent hydrogen is absorbed by the nitric acid with formation of ammonium nitrate.

Arrott Cells (1843).—Platinum, solution of potassium sulphide; porous cup, nitric acid, platinum. Other cells by the same author are: (1) In an outer vessel solution of a salt of protoxide of iron, tin, or manganese associated with a salt of peroxide of the same metal; in the porous cup, nitric acid. (2) In an outer vessel, solution of an alkaline chloride, sulphide, or hyposulphite; in the porous cup, chloric, nitric, or chromic acids.

Matteucci Cells having a Single Metal and Two Liquids (1852).—These cells consist of a glass containing jar, a porous cup, and two platinum plates, one entering the liquid contained in the jar, and the other that in the porous cup. The following liquids operate like zinc in the cell:

> Solution of potassium pentasulphide;
> "   "   "   monosulphide;
> "   " sulphurous acid (saturated);
> "   " sodium hyposulphite;
> "   " potassium sulphite;
> "   " caustic potash;
> "   " ferrous sulphate.

.The following liquids operate like platinum, copper, or carbon in the cell:

Nitric acid, pure and concentrated.

Concentrated solution of chromic acid.

Solution of sulphuric acid 1 part in 8 to 10 parts water.

For the same purpose may be used a layer of lead peroxide on the platinum plate moistened with the above dilute sulphuric acid.

The potash and nitric acid cell was discovered by Becquerel, and De la Rive used lead peroxide in place of nitric acid in the Grove cell. The foregoing cells usually have quite a high E. M. F., but they are not very constant. A single cell (nitric acid and potassium pentasulphide) decomposes water, and hence its E. M. F. is equal to at least 1.5 volts.

Grezel Cell (1884).—Carbon, acidulated water; porous cup, solution of ammonium carbonate, carbon. Here there is a disengagement of carbonic acid and formation of ammonium sulphate.

Woehler and Weber Cell (1841).—Iron, dilute sulphuric acid; porous cup, concentrated nitric acid, iron.

Balsamo Cell.—Iron, dilute sulphuric acid; porous cup, solution of calcium chloride, iron.

. *Napoleon III. Cell.*—(*a*) Copper, dilute nitric acid; porous cup, dilute sulphuric acid, copper. (*b*) Zinc, dilute sulphuric acid; porous cup, tepid water, zinc. These cells, having been invented by the emperor, attracted considerable attention.

. *Regnauld Cell.*—Copper, potash solution; porous cup, copper sulphate solution, copper. E. M. F. = 0.491 volt.

Buff Cells (1857).—(*a*) Aluminium, acidulated water; porous cup, nitric acid, aluminium. E. M. F. with nitric acid of density 1.4 = 1.13 volts. (*b*) Aluminium, potash or soda solution; porous cup, nitric acid, aluminium. E. M. F. = about 1.6 volts. This cell is stronger than either of the forms in which zinc is immersed in potash or aluminium in nitric acid.

(2) CELLS HAVING SOLID DEPOLARIZERS.

If there be placed in a solution of potassium nitrate two plates of platinum one of which is covered with metallic oxide or sulphide, the following results, according to the nature of the substances, are obtained:

The solution is negative* with the following:	The solution is positive with the following:
Minium;	Lead peroxide;
Cuprous oxide;	Ferric oxide;
Stannous "	Argentic "
Zinc "	Stannic "
Silica;	Cupric "
Red sulphide of mercury;	
Silver sulphide;	
Alumina.	(Becquerel, 1849.)

Carbon Electrode Cell (without Metals) of Tommasi and Radiguet (1884) (Fig. 121).—Carbon, salt water; porous partition, lead peroxide, carbon. E. M. F. = 0.6 to 0.7 volt. This cell works only on closed circuit, and as it polarizes rapidly it is suited only to conditions in which an intermittent current is required. So used, its lifetime is exceedingly long, and in fact it will remain in normal condition for many years. It is constructed in two forms.

First model. At the bottom of a rectangular porcelain jar is a carbon plate embedded in a paste of lead peroxide and forming one electrode. The other electrode is a similar carbon plate, covered on its upper side with fragments of retort-carbon. The plates are superposed and separated by a sheet of parchment-paper which divides the jar into two compartments.

Second model. In the middle of a cylindrical glass vessel is a carbon rod covered with a thick layer of lead peroxide and

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* Becquerel's statement is just the reverse of this; but as generally in his researches he regards the zinc as the negative electrode, the transposition of terms is here made to bring them into uniformity with the definitions of this book.

enclosed in a canvas bag which replaces the parchment-paper in the first model. This electrode so enveloped is placed in a perforated tube of carbon. The glass vessel is filled with fragments of retort-carbon and a concentrated solution of sodium chloride to which calcium chloride is added—which last hinders evaporation of the water. The level of this solution should not be above the middle of the jar. The pieces of carbon which are not immersed are covered with calcium chloride.
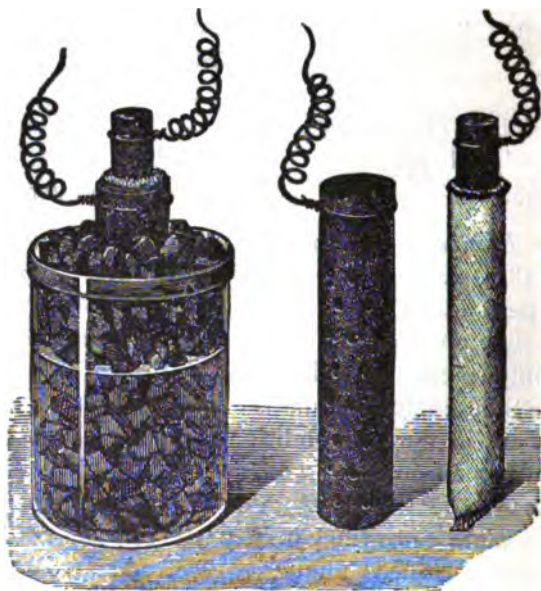
FIG. 124.—TOMMASI AND RADIGUET CELL.

The theory of this cell, according to M. Tommasi (1885) is as follows :

Tscheltzow (1885) has determined that the passage of a molecule of lead protoxide to the state of peroxide disengages 12.14 cal. The heat of formation of anhydrous lead protoxide (PbO) being 51 cal., it follows that the heat of formation of the peroxide (PbO$_2$) is 63.14 cal. Beginning with the

effect caused by the carbon on the water, the occurrences in the cell may be explained as follows :

The carbon decomposing the water, on closed circuit there will be formed carbonic acid and hydrogen will be set free, or

$$C + 2H_2O = CO_2 + 4H.$$
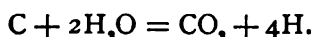
The thermic effects of this reaction are :

$$102.6 \text{ cal.} - 138.0 \text{ cal.} = -35.4 \text{ cal.}$$

On the other hand, in the bag which takes the place of the porous cup there is reduction of the lead peroxide and formation of water, or

$$PbO_2 + 4H = Pb + 2H_2O,$$
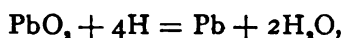
and the thermic effects of this reaction are

$$138.0 \text{ cal.} - 63.14 \text{ cal.} = 74.86 \text{ cal.}$$

The heat resulting from these two reactions is the algebraic sum of their thermic effects, or $74.86 \text{ cal.} - 35.40 = 39.46 \text{ cal.}$ Taking the volt at 46.3 cal., the E. M. F. of the cell is $\dfrac{39.14}{46.3}$ or 0.85 volt ; or at 47.16, as has been proposed by some investigators, $\dfrac{39.14}{47.16} = 0.84$ volt. Direct measurements give 0.6 to 0.7 volt. This difference is easily explained when it is considered that the cell polarizes readily, and that besides carbonic acid, carbonic oxide is also formed, which would tend to diminish the heat produced by the first reaction. Furthermore there are secondary actions, and the phenomena are certainly influenced by temperature, degree of purity of the substances used, etc.

Gresel Cell (1884).—(a) Carbon, $\overset{+}{\text{acidulated}}$ water ; porous cup or parchment-paper partition filled with cupric oxide $(\overset{-}{\text{CuO}})$, carbon. The positive electrode becomes covered on

closed circuit with little bubbles of oxygen, and the negative electrode with reduced copper.

(*b*) Carbon$\overset{+}{}$, diluted hydrochloric acid ; porous cup, slaked lime, carbon$\overset{-}{}$. Reaction :

$$2ClH + CuO = H_2O + Cl_2Ca \text{ (calcium chloride)}.$$
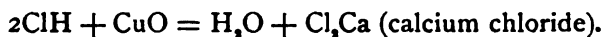
Grezel Cell (1884).—Copper$\overset{+}{}$, acidulated water ; porous cup or parchment-paper bag filled with cupric oxide, copper. The enclosed metal becomes covered with reduced copper, the positive electrode with binoxide (CuO). When both electrodes become covered with the same quantity of binoxide the current stops.

CHAPTER XII.

CELLS HAVING TWO LIQUIDS. (*Continued.*)

III. PRACTICAL DATA AND TABLES.

Table showing the E. M. F. of certain Two-electrolyte Cells.
(*E. Becquerel*, 1855).—The sign $+$ in the following table indicates that the electric effect due to the action of the two solutions is in the same direction as that which is produced on the negative electrode; the sign $-$, that it is in the opposite direction. Thus in every case it is necessary, in order to determine the E. M. F. of the cell, to take account of the indicated signs algebraically.

Disposition of the Cells.	E. M. F.			
	Due to the Action on the Positive Electrode.	Due to the Action on the Negative Electrode.	Due to the Action of the Solutions.	Of the Cell.
	volt.	volt.	volt.	volt.
Pure zinc, water acidulated to $\frac{1}{10}$ sulph. acid / Platinum, ordinary nitric acid 36° B.	1.349	....	$+0.357$	1.630
ZincHg, $\frac{1}{10}$ acidulated water / Platinum, nitric acid	1.326	....	$+0.357$	1.683
Pure zinc, $\frac{1}{10}$ acidulated water / Copper, sat. sol., copper sulphate	1.273	-0.262	-0.093	0.918
ZincHg, $\frac{1}{10}$ acidulated water / Copper, sat. sol., copper sulphate	1.326	-0.262	-0.093	0.969
Pure zinc, $\frac{1}{10}$ acidulated water / Platinum, sat. sol., platinum chloride	1.351	....	$+0.131$	1.483
ZincHg, $\frac{1}{10}$ acidulated water / Platinum, chlorine water	1.406	....	$+0.643$	2.040
ZincHg, 25% potash sol. / Platinum, nitric acid	1.377	....	$+0,765$	2.142
Pure zinc, 20% persulphide of potassium / Platinum, nitric acid	0.229	....	$+1.232$	1.462

ELECTROMOTIVE FORCES OF CERTAIN DEPOLARIZERS.
(E. BECQUEREL, 1855.)

The numbers in the following table representing E. M. F. are, in relation to that of pure non-amalgamated zinc, equal to 1.35 volts and acting in opposite direction : the action of pure zinc, in other words, being — 1.35 volts. The determinations have been made at a temperature of about 14° C.

Substances.	E M. F., that of zinc being — 1.35 volts.
Liquids in presence of water with 10% sulph. acid :	
Water oxygenated with 12 vols. of oxygen...+ 0.127 volt.	
Saturated sol. of platinum chloride..........+ 0.134 "	
Concentrated nitric acid...................+ 0.345 "	
Chromic acid ....+ 0.474 "	
Sat. chlorine water. . . ..+ 0.644 "	
Peroxide in presence of water with 10% sulph. acid :	
Ordinary manganese peroxide..............+ 0.330 "	
Electrolytic manganese peroxide on platinum+ 0.590 "	
Pure lead peroxide in powder...............+ 0.812 "	
Electrolytic lead peroxide on platinum......+ 0.858 "	

The E. M. F. of a constant-current cell formed of an oxidizable metal in water containing 10% sulphuric acid, and of platinum surrounded with one of the substances contained in the table is obtained by adding to the numbers in the column of acidulated water of the table on page 146 the numbers of the foregoing table. Thus the E. M. F. of the couple containing potassium amalgam and electrolytic lead peroxide is 2.341 volts + 0.858 volt = 3.199 volts.

ELECROMOTIVE FORCE OF THE GROVE CELL.   (POGGENDORFF.)

Liquid acting on the Zinc.	Liquid acting on the Platinum.	E. M. F.
Sulphuric acid, D. = 1.136	Fuming nitric acid	1.955 volts.
" " " = 1.136	Nitric acid, D. = 1.33	1.809 "
" " " = 1.060	" " " = 1.33	1.730 "
" " " = 1.136	" " " = 1.19	1.681 "
" " " = 1.060	" " " = 1.19	1.631 "
Solution of zinc sulphate,	" " " = 1.33	1.905 "

ELECTROMOTIVE FORCE OF CERTAIN CELLS OF THE GROVE TYPE.   (BEETZ, 1853.)

		volts.
Zinc, dilute sulphuric acid :	Nitric acid, platinum	1.844
	Hydrochloric acid, platinum	1.481
	Potassium chlorate, "	1.626
	Sodium chloride, "	1.618
	" bromide, "	1.567
	" iodide, "	1.102
	Dilute sulphuric acid, "	1.662
	" " " "	1.577

E. M. F. OF CERTAIN TWO-LIQUID CELLS.   (JOULE.)

	volts
Zinc^{Hg}, dilute sulph. acid; porous cup, nitric acid, platinum	1.83
Iron " " " " " " " "	1.37
Copper, " " " " " " " "	0.89
Silver, " " " " " " " "	0.52
Platinum, " " " " " " " "	0.36
Zinc^{Hg}, sol. of sulphate of soda; porous cup, nitric acid, platinum........	1.83
Iron, " " " " " " " "	1.44
Copper, " " " " " " " "	0.90
Silver, " " " " " " " "	0.52
Platinum, " " " " " " " "	0.17
Zinc^{Hg}, sol. of sodium chloride; porous cup, nitric acid, platinum........	1.94
Iron, " " " " " " " "	1.43
Copper, " " " " " " " "	1.13
Silver, " " " " " " " "	0 93
Platinum, " " " " " " " "	0.54
Zinc^{Hg}, sol. of potash; porous cup, nitric acid, platinum.................	2.29
Iron, " " " " " " "	1.65
Copper, " " " " " " "	1.17
Silver, " " " " " " " . "	0.45
Platinum, " " " " " " "	0.30
Amalgam of potassium, " " " " "	2.95
Zinc^{Hg}, sol. of sulphate of soda; porous cup, copper sulphate, copper....	1.02
Iron, " " " " " " " "	0.58
Copper " " " " . " " " "	0.08
Zinc^{Hg}, dilute sulph. acid; porous cup, copper sulphate, copper..........	0.98
Iron, " " " " " " " "	0.48
Copper, " . " " " " " " "	0.04

volts.

Zinc^{Hg}, sodium chloride; porous cup, copper sulphate, copper............ .. 1.04
Iron,   "   "   "   "   "   "   " 0.54
Copper,   "   "·   "   "   "   "   " 0.27
Ferrohydrate of potash,   "   "   "   "   " 0.66
Copper,   "   "   "   "   "   "   " 0.52

E. M. F. OF CERTAIN TWO-LIQUID CELLS. (E. REYNIER.)

volts.

Daniell standard, ordinary zinc, zinc sulphate (D. = 1.09), copper, copper sulphate (D. = 1.16)............ 1.068

Same, with very small addition of sulphuric acid in the copper sulphate................................. 0.993

Same, with very small addition of sulphuric acid in both liquids..................................... 1.929

Same, with a small addition of tartaric acid in the copper sulphate................................. 1.015

Ordinary zinc, potash lime (potasse à la chaux) (solution 30%), copper, copper sulphate (D. = 1.116)........ 1.511

Ordinary zinc, solution of soda and potash (potash 175, soda 250, water 1000), copper, copper sulphate (D. = 1.16)..................................... 1.661

Ordinary zinc, solution of soda (Reynier's formula), copper, copper sulphate (Reynier's formula).......... 1.473

Same, with amalgamated zinc....................... 1.500

Iron, commercial iron sulphate (D = 1.20), copper, copper sulphate (D. = 1.16)....................... 0.711

E. M. F. OF CERTAIN TWO-LIQUID CELLS. (RAOULT, 1863.)

I.	E. M. F.	
	With Platinum. volt.	With Gold. volt.
+ Copper, conc. sol. of copper sulphate − Platinum or gold, nitric acid	0.518	0.594
+ Copper, conc. sol. of copper sulphate − Platinum or gold, sulphuric acid	0.529	0.560
+ Copper, conc. sol. of copper sulphate − Platinum, hydrochloric acid	0.270	0.453
+ Copper, conc. sol. of copper sulphate − Platinum, acetic acid	0.291	0.324

	II.	E. M. F. With Platinum. volt.	With Gold. volt.
+ Copper, conc. sol. of copper sulphate − Platinum or gold, sodium chloride		0.237	0.097
+ Copper, conc. sol. of copper sulphate − Platinum or gold, barium chloride		0.256	0.140
+ Copper, conc. sol. of copper sulphate − Platinum or gold, zinc chloride		0.291	0.183
+ Copper, conc. sol. of copper sulphate − Platinum or gold, ferrous chloride		0.151	0.151
+ Copper, conc. sol. of copper sulphate − Platinum or gold, stannous chloride		0.032	0.021
+ Copper, conc. sol. of copper sulphate − Platinum or gold, cupric chloride		0.421	0.334
+ Copper, conc. sol. of copper sulphate − Platinum or gold, mercuric chloride		0.50	0.442
+ Copper, conc. sol. of copper sulphate − Platinum or gold, platinic chloride		0.583	0.572

III.

+ Copper, conc. sol. of copper sulphate − Platinum or gold, sodium sulphate		0.118	0.0864
+ Copper, conc. sol. of copper sulphate − Platinum or gold, zinc sulphate		0.237	0.097
+ Copper, conc. sol. of copper sulphate − Platinum or gold, ferrous sulphate		0.140	0.108
+ Copper, conc. sol. of copper sulphate − Platinum or gold, copper sulphate		0.291	0.237

IV.

+ Copper, conc. sol. of copper sulphate − Platinum or gold, sodium nitrate		0.280	0.151
+ Copper, conc. sol. of copper sulphate − Platinum, barium nitrate		0.237	0.162
+ Copper, conc. sol. of copper sulphate − Platinum or gold, zinc nitrate		0.302	0.216
+ Copper, conc. sol. of copper sulphate − Platinum or gold, lead nitrate		0.378	0.216
+ Copper, conc. sol. of copper sulphate − Platinum or gold, copper nitrate		0.410	0.356
+ Copper, conc. sol. of copper sulphate − Platinum or gold, silver nitrate		0.475	0.583

V.

E. M. F.

+ Platinum, conc. sodium nitrate
− Platinum, silver nitrate in 10 parts water } ....0.0864 volt.

+ Gold, conc. sodium nitrate
− Gold, silver nitrate in 10 parts water } ....0.421 "

+ Platinum, sodium acetate $\frac{1}{10}$ sol.
− Platinum, conc. silver acetate } ....0.226 "

+ Gold, sodium acetate $\frac{1}{10}$ sol.
− Gold, conc. silver acetate } ....0.464 "

VI.

	E. M. F.	
	With Platinum. volt.	With Gold. volt.
+ Copper, conc. sol. of copper sulphate − Platinum or gold, sodium acetate }	....0.194	0.075
+ Copper, conc. sol. of copper sulphate − Platinum or gold, barium acetate }	....0.205	0.097
+ Copper, conc. sol. of copper sulphate − Platinum or gold, zinc acetate }	....0.226	0.108
+ Copper, conc. sol. of copper sulphate − Platinum or gold, lead acetate }	....0.324	0.194
+ Copper, conc. sol. of copper sulphate − Platinum or gold, copper acetate }	....0.356	0.216
+ Copper, conc. sol. of copper sulphate − Platinum or gold, silver acetate }	....0.421	0.540

EFFECT OF (I) AGITATION OF THE ELECTRODES,
(II) PRESENCE OF THE AIR,
(III) DEGREE OF CONCENTRATION OF
THE ELECTROLYTE,
(IV) TEMPERATURE

ON THE E. M. F. OF CERTAIN TWO-LIQUID CELLS.
(RAOULT, 1863.)

I. AGITATION OF THE ELECTRODES.

−	+	volt.
Copper, conc. sol. } copper sulphate }	{ Copper at rest in 10% sol. of } { hydrochloric acid }	0.324
Same	Copper agitated in same solution	0.378

volt.

Copper, conc. sol. copper sulphate } { Copper at rest in 10% sol. potassium cyanide } 0.339

Same — Copper agitated in same solution 0.317

+ —
Copper, conc. sol. copper sulphate } { Platinum at rest in chlorine water } 0.915

Same } { Platinum agitated in chlorine water. } 0.972

II. PRESENCE OF THE AIR.

— + volt.

Copper, conc. sol. copper sulphate } { Platinum, pure water deprived of air } 0.005

+
Same Platinum, pure water aerated... 0.162

+
Same { Gold, pure water deprived of air } 0.0864

+
Same Gold, pure water aerated...... 0.0756

+
Same { Platinum, 10% sol. of sulphuric acid deprived of air } 0.540

+
Same { Platinum, 10% sol. of sulphuric acid aerated } 0.507

+
Same { Platinum, 25% sol. of sodium chloride deprived of air } 0.410

+
Same { Platinum, sol. of sodium chloride aerated } 0.432

It will be seen from the foregoing that the presence of air, which modifies so considerably the E. M. F. of water, has but little effect on the electromotive action of suitably concentrated solutions.

III. DEGREE OF CONCENTRATION OF ONE OF THE ELECTROLYTES.

+ — volt.

Copper, conc. sol. copper sulphate } { Platinum, concentrated nitric acid } 0.810

Same Platinum (acid 1, water 5)...... 0.702

Same Platinum (acid 1, water 10)..... 0.702

		volt.
Copper, conc. sol. copper sulphate	Platinum (acid 1, water 10).....	20.57
Same	Platinum, platinum chloride (chloride 1, water 5)	0.572
Same	Platinum, platinum chloride (chloride 1, water 20)	0.594
Same	Platinum, platinum chloride (chloride 1, water 80)	0.604
Same	Platinum, platinum chloride (chloride 1, water 320)	0.637
Same	Platinum, platinum chloride (chloride 1, water 1000)	0.637
Same	Platinum, sodium sulphide (sulphide 1, water 10)	1.026
Same	Platinum, sodium sulphide (sulphide 1, water 40)	1.026
Same	Platinum, sodium sulphide (sulphide 1, water 160)	0.907
Same	Platinum, sodium sulphide (sulphide 1, water 640)	0.669
Same	Platinum, sodium sulphide (sulphide 1, water 2560)	0.367

From which it appears that the E. M. F. due to the contact of the two solutions varies very slightly with their degree of dilution.

−	+	
Platinum (platinum chloride 1, water 5)	Platinum in pure water deprived of air	0.572
Platinum (chloride 1, water 100)	Same	0.615
Platinum (chloride 1, water 1000)	Same	0.615
Platinum (chloride 1, water 10,000)	Same	0.594

Whence it results that the electric effect is not at all due to the affinity of the solution for water.

IV. EFFECT OF TEMPERATURE.

Ordinary Temperature.		T° C.	volt.
+	−		
Copper, conc. sol. copper sulphate	Platinum (sodium chloride 1, water 10)	40°	0.324
Same	Same	30°	0.259
Same	Same	·20°	0.270
Copper, conc. sol. copper sulphate	Platinum (nitric acid 1, water 10)	40°	0.594
Same	Same	30°	0.594
Same	Same	20°	0.583
Same	Same	10°	0.594
Same	Same	5°	0.594
Copper, conc. sol. copper sulphate	Platinum (platinum chloride 1, water 10)	70°	0.658
Same	Same	50°	0.626
Same	Same	30°	0.615
Same	Same	10°	0.594

ELECTROMOTIVE FORCE OF THE PLATINUM-PLATINUM COUPLE, EACH ELECTRODE ENTERING A DIFFERENT LIQUID. (RAOULT, 1863.)

		E. M. F. after an immersion of		
		6 sec. volt.	1 min. volt.	5 min. volt.
Platinum, 10% sol. sulphuric acid	Platinum, pure water	0.572	0.550	0.626
Platinum, 10% sol. nitric acid	Same	0.680	0.723	0.745
Platinum, pure water	Platinum, potas. cyanide	0.237	0.280	0.399
Same	Plat., sodium hyposulphite	0.118	0.226	0.237

DIFFERENCE OF POTENTIAL BETWEEN A METAL AND LIQUIDS OF DIFFERENT CONCENTRATION. (E. KITTLER, 1882.)

The several liquids tested, placed in glasses, are put in communication by means of siphons closed with parchment and filled with the liquid of which the specific gravity is lowest.

   1. The difference of potential at the extremities of the chain

$$Cu \mid L + L \mid SO_4Cu + SO_4Cu \mid Cu,$$

in which L represents a concentrated solution in water of one of the chlorides noted in the following table, is:

Chlorides of		E. M. F.
Ammonium,	$ClNH_4$	0.343 volt.
Potassium,	ClK	0.340 "
Lithium,	$ClLi$	0.332 "
Calcium,	Cl_2Ca	0.328 "
Sodium,	$ClNa$	0.326 "
Strontium,	Cl_2Sr	0.313 "
Magnesium,	Cl_2Mg	0.297 "
Barium,	Cl_2Ba	0.271 "
Manganese,	Cl_2Mn	0.260 "
Nickel,	Cl_2Ni	0.249 "

   The order in which the chlorides noted are arranged remains the same if distilled water be substituted for copper sulphate. This last proposition has been verified in the case of the chlorides $ClNH_4$, ClK, Cl_2Ni.

   2. The E. M. F. of the cell diminishes with the degree of concentration of the saline solution.

   3. In the preceding chain the current is directed from the chloride to the sulphate, or from the chloride to the water; from the concentrated solution to the dilute solution.

   4. The solutions of the chlorides noted in the preceding table follow Volta's law.

   5. The order of the chlorides in the above table, in which the E. M. F.'s constantly diminish from first to last, is not the same when, in the foregoing chain, copper sulphate is replaced by acidulated water.

   6. The solutions of the chlorides in contact with sulphuric acid do not follow Volta's law of tensions.

   7. The difference of potential at the extremities of the liquid chain

$$SO_4Cu \mid L + L \mid SO_4H_2 + SO_4H_2 \mid SO_4Cu$$
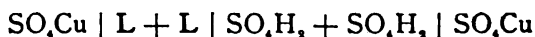
(in which SO_4Cu and SO_4H_2 represent respectively a like solution of copper sulphate and water containing the same proportion of sulphuric acid) changes considerably with the degree of concentration of the chloride L.

E. M. F.'S OF AMALGAMS OF ZINC AND POTASSIUM. (REGNAULD, 1855.)

[Liquid zinc amalgam $\frac{1}{10}$, porous cup ; copper sulphate, copper.]

		volt.
Liquid zinc amalgam $\frac{1}{10}$ Solution of zinc sulphate	Copper Sol. copper sulphate	0.97
Liquid zinc amalgam $\frac{1}{100}$ Solution of zinc sulphate	Copper Sol. copper sulphate	0.97
Liquid zinc amalgam $\frac{1}{100}$ Solution of zinc sulphate	Copper Sol. copper sulphate	0.97
Liquid potas. amalgam $\frac{1}{100}$ Solution of sodium chloride	Platinum Platinum chloride	2.23
Liquid potas. amalgam $\frac{1}{1000}$ Solution of sodium chloride	Platinum Platinum chloride	2.22

E. M. F.'S PRODUCED BY THE ACTION OF TWO PLATES OF THE SAME METAL PLACED, ONE IN DISTILLED WATER, THE OTHER IN SEA WATER. (T. ANDREWS, 1884.)

Metals.	E. M. F.
Forged iron, rolled and polished	0.054 volt.
Forged iron, hammered................	0.017 "
Soft Bessemer steel....................	0.024 "
Hard Bessemer steel.................. ...	0.110 "
Soft Siemens-Martin steel........... ...	0.038 "
Hard Siemens-Martin steel.......	0.066 "
Cast-steel (soft)	0.026 "
Cast-steel (hard).	0.047 "
Cast-iron No. 1, polished..............	0.027 "
Cast-iron No. 1, rough................	0.035 "
Cast-iron No. 2, polished..............	0.009 "
Forged iron, covered with magnetic oxide	0.028 "

ELECTROMOTIVE FORCE. RESISTANCE AND UNPRODUCTIVE CONSUMPTION OF CERTAIN VOLTAIC CELLS.

(A. MAURI, 1881.)

Cells.	E M.F.'s to Circuit.		Average Resistance.	Monthly Unproductive Consumption.	
	Open.	Closed.		Zinc.	Exciting Compound.
	volt.	volt.	ohm.	grs.	
Daniell...................	1.079	0.98	5.0	14	SO_4Cu 53 grams
Mauri....................	1.150	1.05	6.5	0	" 0 "
Callaud	0.970	0.97	6.5	20	" 76 "
Siemens-Halske...........	0.970	0.98	7.0	6	" .22 "
Copper sulphate and sulphur	1.34	1.25	4.0	0	" 0 "
" " " " .	1.1	0.95	4.0	0	" 0 "
Marié-Davy........... ...	1.5	1.35	7.0	5	SO_4Hg 22.5 "
Duchemin.................	1.6	1.4	7.0	6	Cl 65 "
Bacco....................	1.6	1.4	7.0	.6.	NO_3H 10 g., SO_4H_3 9 g.
Leclanché................	1.4	1.1	4.0	1	O
Salleron and Renoux.......	1.6	1.4	3.5	9	SO_4H_3 15g., ClO_3K 4.5g.
Bunsen...................	1.9	1.7	2.0	15	SO_4H_3 20g., NO_3H 30g.
Delaurier.................	2	1.7	3.0	10	$Cr_2O_7K_2$ 15g., SO_4H_3 35g.
Chromic acid (Mauri).	2.04	1.7	2.5	0	SO_4H_2 30 g.
Grenet...................	1.9	1.6	1.5	0	
Iodine chloride...........	1.7	1.5	2.5	0	ClH 30 g.
				iron.	
Aqua regia................	1.25	1.15	1.0	25	ClH 50g., NO_3H 28g.
Ferric sulphate............	1	0.92	4.0	4	NO_3H 4.528, SO_4H_3 6g.
Gérardin-Ponci...........	1.05	0.92	7.0	4	Cl 4.5

VARIATION OF E. M. F. WITH TEMPERATURE. (F. LENDIG, 1864.)

1. The E. M. F.'s are variable with temperature for certain elements (copper in copper sulphate, zinc in zinc sulphate, non-amalgamated zinc in sodium chloride), and not variable for others (zinc in sulphuric acid).

2. The direction of the variation is not always the same. For copper the E. M. F. diminishes when the temperature increases; for zinc (non-amalgamated) in sodium chloride it augments.

3. The variation of the E. M. F. is not always proportional to the variation of temperature between 2° and 85° C.

4. Conformably to 1 and 2, the E. M. F. of the Daniell element is variable when the zinc is immersed in dilute sulphuric acid or in a sodium chloride solution.

CHAPTER XIII.

HEAT CELLS.

CELLS in which heat energy is converted into electrical energy are of three principal types:

1. Those in which the heat acts upon the materials of the call by causing fusion or decomposition.

2. Those in which heat operates to set free chemical affinities whereby the cell is caused to operate, the regeneration after exhaustion taking place at a lower temperature.

3. Thermo-chemical cells, or those in which a difference of potential is maintained- between two bodies immersed in a liquid by keeping one plate at a higher temperature than the other.

General Considerations (Schieble, 1890).—" With primary batteries, the efficiency, i.e., the energy furnished as current, in terms of that in the materials consumed, is much higher than the efficiency of a steam-dynamo plant. At first thought the electrical energy would be taken as equal to that of the heat of combination of the elements. But F. Braun, Czapski, Gochel, and Jahn* have shown that the relation between the two depends on the individual processes in the cell. A given process may under varying circumstances, while causing the same heat of formation, produce different electromotive forces. It is true that for many of the common reactions the electrical energy produced is practically equal to that of the heat of combination, and may be calculated accordingly. But, as the above-mentioned German physicists have shown, this equality

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* Wiedemann's Annalen d. Phys. u. Chem., Bd. XVI., XXI., XXIV., and XXVIII., respectively.

is not a general one, as Julius Thomsen* and others held it to be. Hence the theoretical efficiency of conversion is not in every case 100 per cent, though it may be very nearly as high. In calculating the working efficiency, as defined above, the known energy of combination of the materials consumed forms the starting point. W. Peukert found the efficiency of the Daniell cell to be 47.7 per cent, that of a Bunsen 59.1 per cent. Prof. Crocker found a bichromate battery solution to have 45 per cent efficiency, and thought that of a copper sulphate solution might be 80–90 per cent. If 75 per cent could uniformly be reached, this would place the battery equal to the dynamo plant, if costing ten or fifteen times as much. But at present electric lighting from batteries costs (roughly) 50 cents per horse-power hour, against 2 cents for that from steam dynamos, or twenty-five times as much. What makes the primary battery lighting so expensive is that recharging means renewing costly elements, a partial repetition of the first cost.

" The great requirement for a heat cell is a chemical action readily and perfectly reversible by heat. Since gases are very poor conductors, this reaction must take place in the wet, i.e., either in solution or in presence of a conducting liquid. Then, too, the element which is to form the attacked electrode must preferably be a solid; although a liquid, separated from the solution either by the difference in their specific gravities or by a porous partition, would do. Such a reaction would probably meet the case. In looking for it whole classes of salts may be excluded for their known common properties, thus narrowing the search."

(1) CELLS IN WHICH THE HEAT ACTS UPON THE MATERIALS OF THE CELL, BY CAUSING FUSION.

Becquerel Cells.—Electrical currents obtained by taking a melted salt as an electrolyte were investigated by A. C. Bec-

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* Original account of experiments in Poggendorff's **Annalen.** English abstract of same in *Scientific American Supplement,* No. 279.

querel. The setting free of the electricity accompanied either combustion of the carbon, or oxidation of different metals at the expense of the electrolyte.

One of the arrangements consisted of melting potassium nitrate in a platinum vessel and plunging therein a rod of carbon the point of which was brought to a state of incandescence. By another method, called a pyro-electric couple, two different metals, a bar of iron and another of copper, were plunged into melted silicate, e.g., into a fused mixture of glass and carbonate of soda. At the ends of the two bars was obtained an electric current four times weaker than the current from a Bunsen battery. There was, therefore, an electromotive force of about one-half volt.

Jablochkoff Heat Cell (1877).—A cylindrical vessel of cast-iron filled with melted nitrate of potash or soda serves both as the containing receptacle and as the positive electrode. (The alkaline nitrates melt at about 200° C., but do not decompose until at from 1000° to 1200° C. Up to this point not only do they not attack metal vessels which contain them, but they appear, on the contrary, to have the singular property of preventing oxidation by fire, or at least of retarding the same considerably.) The coke is held by an iron wire which also serves as a terminal. With the nitrate in a fused state a current of E. M. F. from 1 to 2 volts is produced. If instead of nitrate in fusion an aqueous solution of the salt be employed, the poles are reversed. In fact, in an iron-carbon couple using a solution of soda or potash nitrate the iron is positive and acts like the zinc in the ordinary cell.

Brard " *Brick* " (1882).—This is an agglomerate of ordinary carbon on which is placed a tablet composed of a mixture of nitrate of potash and cinders and separated by an interposed sheet of asbestos paper. The poles are metallic rods which traverse the carbon and nitrate and protrude from one end of the " brick." If the end of the brick opposite to the terminals be placed in the fire, the carbon becomes red hot, the nitrate melts and the current is established, weak at first but gradually stronger, until finally a maximum is reached which remains

constant as long as the intensity of combustion is kept uni-
form.   A small brick 15 cm. long, 3 cm. wide and thick, weigh-
ing 220 grams, of which 120 grams is nitrate of potash and
65 grams cinders, burns for nearly two hours giving during the
whole period a current of from 0.9 to 1.2 volts through a re-
sistance of from 1.2 to 0.8 ohm.   The resistance of this ele-
ment, cold, is 104.5 ohms.

Crum Heat Cell.—Carbon; iron, black iron oxide fused.
The carbon is attacked.

Edison Heat Cell.—The method consists in employing car-
bonaceous material for the soluble electrode of a generating
cell, and using as an active agent oxides, salts, or compounds
of elements by the decomposition of which the carbonaceous
material will be acted upon at high temperatures.   Heat is
applied externally, and the negative electrode of the cell is
made of a substance which in the presence of carbon at high
temperatures is not attacked to any great extent by the active
material employed.

Fig. 125 shows the apparatus.   *A* represents a furnace for
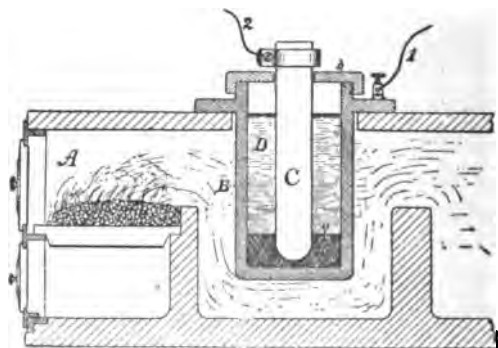
FIG. 125.—EDISON HEAT CELL.

heating the iron melting-pot *B*, and *C* is a cylinder of carbona-
ceous material resting on the fire-clay block *a*.   The cover of
the pot is also of fire-clay.   The circuit connections 1 2 are
made with the pot and carbon cylinder.   The heat of the fur-
nace fuses the oxide at the same time that it raises the carbon

to a temperature at which it combines rapidly with oxygen. A reduction of the oxide takes place, the oxygen combining with the carbon and forming carbon monoxide, which passes off and may be conducted to the combustion-chamber of the furnace and used for fuel, it being burned to carbonic acid, while the metal is carried to the other electrode and deposited upon the walls of the containing vessel. During the oxidation of the carbon an electric current flows through the circuit of the cell. The product of the reduction of the oxide may be reoxidized and used over again as the active agent of the cell.

Langhaus Heat Cell (Figs. 126, 127, 128).—In the Jablochkoff and Becquerel couples, in which carbon is employed for the purpose, a large quantity of the heat set free by the reaction is lost. The same is the case with the process that consists in separating metals from their oxides by carbon, or from their sulphides by means of some other metal.

Mr. Langhaus proposes to use this waste heat in the production of an electric current. The apparatus devised by him for this purpose is shown in the annexed figures. An earthen vessel, *a*, contains a crucible of marble or carbonate of magne-
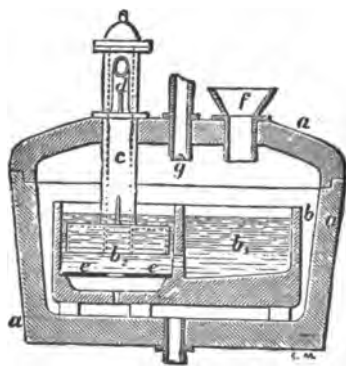
FIG. 126.—LANGHAUS HEAT CELL.

sia divided into two compartments by a partition that contains an aperture. The compartment *b* contains the oxides or sulphides, which, when melted, pass into the other compartment.

Over this latter there is fixed a metallic cylinder, C, which is provided with a piston, and which widens out into a capsule below.   This cylinder, again, carries a lateral tube, d.

Finally, under the widened portion of C there is a metallic disk, e, connected with two supports, e, e_1, provided with terminals on the cover of the apparatus.   The apparatus having been filled through the funnel f with the mass of oxides, and the latter having been melted by the burner g, the carbon is introduced through the tube d.   The carbon is then compressed by the piston, and, being lighter than the molten mass, enters the wide portion of the cylinder C.   A violent reaction then occurs, leading to the reduction of the oxidized mass.

The great quantity of heat liberated under these circumstances is capable of producing an electric current.   The com-

FIG. 127.   LANGHAUS HEAT CELL.   FIG. 128.
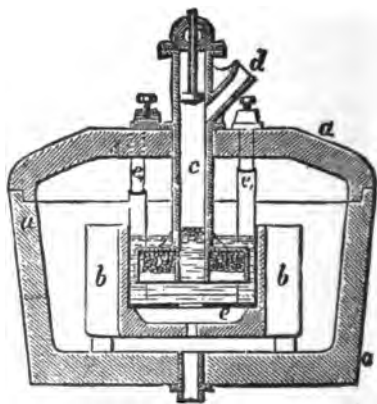
munications being established as shown in Fig. 125, we have a complete circuit formed of the cylinder C of the carbon, of the molten mass, of the disk c, of the supports e, e_1, and of the external circuit.

We have here, then, the proper conditions for the production of an electric current, as two different bodies, carbon and metal, are in contact with a decomposable liquid.

The current produced is very constant, since, in this case, no appreciable polarization can occur.   If, for example, we

take oxide of lead and carbon, a disengagement of carbonic oxide will ensue, but in consequence of the high temperature it will not be able to fix itself upon the carbon, and, moreover, the deposit of metallic lead upon the disk will not cause any polarization. By means of the piston it is possible to renew the carbon without interfering with the operation of the apparatus.

The advantage of this process is evident, since, in addition to the reduction of the metallic oxides or sulphides, it permits of utilizing under the form of electricity the excess of heat necessary to the reduction.

Fabingi and Farkas Heat Cell (1888).—This consists of a small platinum vessel coated on the inside with a compound having the empirical composition $Na_4H_{18}Pt_4O_{11}$, and which is formed by heating the platinum in contact with caustic soda. The vessel is filled with fused caustic soda maintained in a fluid condition by means of a small gas jet. The positive electrode consists of platinum, the negative one of gas carbon. On closing the circuit the E. M. F. soon assumes a steady value, as the carbonate of soda produced is continuously eliminated and deposited in a crystalline form on the free surfaces of the electrodes. The E. M. F. depends on the temperature, but the temperature coefficient is so small that with an ordinary gas flame the E. M. F. may be maintained sensibly constant for several hours. Large and sudden alterations in the external resistance only cause a momentary change in the E. M. F., which almost immediately returns to its original value.

(2) CELLS IN WHICH THE HEAT OPERATES TO SET FREE CHEMICAL AFFINITIES WHEREBY THE CELL IS SET IN ACTION— REGENERATION AFTER EXHAUSTION TAKING PLACE AT A LOWER TEMPERATURE.

Case Cell (1886).—The double reactions here utilized were discovered by Sir Henri Loewel. Plates of tin and platinum, forming the electrodes, are immersed in a solution of chromic chloride, which has no action on the plates at ordinary temper-

ature, so no current is generated. When heated the liquid becomes active, and part of one of its elements, chlorine, leaves the chromic chloride, goes over and temporarily combines with the tin, forming a protochloride of tin. The chemical action generates an electric current, but soon the tin is all converted into chloride and the current ceases. When the cell is cooled, this temporary combination of the chlorine and tin is broken up, and the chlorine returns to the chromium protochloride. The tin being set at liberty, falls as a metallic precipitate to the bottom of the cell in the form of crystals, ready to renew the combination when the cell is again heated. The author considers that when electric currents are generated the heat absorbed by the solution of the tin is in excess of that generated by the precipitation by the equivalent of the electrical energy developed, and that the possible excess is governed by the second law of thermo-dynamics. If the cell works between 80° and 180° F., the E. M. F. at the higher temperature is about 0.26 volt ; the efficiency is less than 16 per cent, as the possible efficiency $= \dfrac{T-t}{T}$ reckoned from absolute zero, or $\dfrac{638° - 538°}{638°} = .157.$

In practice, probably nothing like 16 per cent could be utilized. Results of experiments upon this cell in commercial form are wanting.

(3) THERMO-CHEMICAL CELLS.

In this type of cell a difference of potential is maintained between plates of the same metal immersed in a solution of a salt of the metal, by heating one plate more than the other. Usually the plate at the higher temperature is the negative electrode in the cell, the current passing through the external circuit from the hot plate to the cold plate ; so that the cold plate corresponds to the zinc in most ordinary forms of voltaic cells. The results given by different investigators on this subject are, however, at considerable variance.

Becquerel states that a warm plate is negative with relation to a cold plate when both are plunged in an alkaline solution; and the reverse is true when the solution is an acid. Also, that, effects being the same on the contact of a cold liquid with a hot one, it is concluded therefrom that the immersion of a hot plate of metal in a liquid heats the liquid surface which surrounds the plate, whence results an electric current due to the reaction of the hot surface on the environing liquid.

According to Matteucci, there is no development of electricity in mercury or liquid amalgams. Whatever current may have been observed he considers to be due to the contact of the metallic wires with the mercury or amalgam, this being directed from the hot to the cold part, as if the wires touched directly without intervention of the liquid. The non-production of the current, he says, is owing, not to the amalgam itself, but solely to its liquid condition. In fact, the crystallized amalgam of bismuth, for example (5 parts of bismuth and 1 part of mercury), possesses a very high thermo-electric power, which is lost in the fused state.

G. Gore (1878) observes that when there are no chemical reactions between the plates and the liquid, the hot metal is positive with relation to the other in alkaline solutions and negative in acid solutions; but that selenic acid, silver nitrate, chrome alum, and the sulphates of nickel, manganese, iron, and copper are exceptions to this rule. When the plate is heated for a short time, the intensity of the current generally augments—sometimes it diminishes. The direction and intensity of the current depend only on the liquid; the nature of the metals being without influence in this regard. With solutions of chrome alum and nickel sulphate and nitrate, the direction of the current may be reversed when the temperature is increased. In some instances, as with nickel bromide, the intensity reaches a maximum at a definite temperature. The results obtained by Gore accord with those determined by Pfaff, Buff, Pictet, and others.

Various Thermo-chemical Cells.

Pacinotti Cell (1865).—Two seamless vessels of copper are placed concentrically, and the interval between them is filled with a concentrated solution of copper nitrate. The exterior vessel is cooled in ice, and the interior is heated by a current of steam. The current developed is directed from the exterior hot copper toward the cold copper, and the E. M. F. increases quite regularly with the difference of temperature. On replacing the copper vessels with zinc vessels and the copper nitrate with zinc nitrate, Pacinotti has determined an E. M. F. equal to about 1 Daniell when the difference of temperature is 180° C. The heated vessel is positive.

Becquerel Cell (1866).—Two plates of copper are immersed in a solution of copper sulphate. One plate is cooled to 0°, the other to 100° C. E. M. F. = 0.054 Daniell.

Bleekrode Cell (1869).—Two test-tubes are connected by a siphon. One is cooled on ice, the other heated in a bath, and both are filled with the same metallic solution and provided with electrodes of the metal entering into the solution. The current goes from the hot electrode to the cold one when copper sulphate, silver acetate, or zinc chloride is used. E. M. F. increases rapidly with the temperature.

Hellesen Cell (1877).—Two test-tubes are connected near their mouths by a short pipe and contain electrodes of copper arranged one over the other. The tubes are filled with a copper sulphate solution. When the tube which has the electrode in its upper portion is heated over an alcohol lamp, a quite energetic current is produced, and the electrode thus heated becomes covered with a copper deposit. The same result is obtained by using as electrodes platinum and lead, and as electrolyte dilute sulphuric acid. With metals which are good conductors of heat the following disposition may be employed : On the edge of a glass filled with copper sulphate solution is fixed a copper plate bent over so as to touch on one side the solution and to expose the other to the source of

heat. The other plate is immersed in the vessel and is con-
nected to the first by a wire covered with gutta percha. A
quite strong current is obtained on heating the exposed plate.
Faraday attempted this experiment with a U-tube, but did not
obtain significant results, probably because the difference of
temperature of the liquid around the electrodes was insuffi-
cient.

Riatti Cell (1884).—A wooden or porcelain receiver trav-
ersed by two copper tubes fixed at a certain distance apart.
Through the upper tube circulates steam at 150° C., 75 lbs.
pressure, and through the lower tube cold water. The re-
ceiver contains copper sulphate solution. The circuit being
closed, the copper of one tube is dissolved and is deposited on
the other.

Powell Cell.—Copper plates in a copper sulphate solution.
A horizontal plate is placed in the bottom of the cell, with
which one conductor connects. Another copper plate with a
copper tube attached to its centre is suspended so that its un-
der surface touches the surface of the solution. The bottom
of the copper tube is perforated, making it a rose-burner. Gas
is conducted in through the tube, lighted at the openings, and
the small flames heat copper wires riveted to the copper plate.
E. M. F. = 0.035 volt at a difference of temperature of 50° C.
between the upper and lower plates. Current goes from the
warm to the cold plate through the external circuit.

*Thermo-electric E. M. F.'s produced by the Contact of a
Metal and a Liquid.*—The most extended investigations on
this subject were made by M. Bouty in 1880 (*Journal de Phy-
sique*, 1880, p. 229). His experimental cell consists of two
small test-tubes, each containing a thermometer and connected
by a capillary siphon. In the tubes are immersed " pieces of
the same metal wire broken in two," the wire being covered
with a protecting varnish except at the ruptured extremities.
One tube is heated in a *bain-marie*, the other is covered in an
earthenware pot in which cold water circulates.

The following table gives the principal results obtained by

Bouty. For all metals the hot pole is positive outside the cell.

Metal.	Liquid.	Thermo-elec. coefficient. (E. M. F. for diff. of temp. of 1°.) Daniell.	Average for each Metal. Daniell.
Platinum	Platinum chloride	0.000735	0.000735
Copper	Copper sulphate	0.000688	0.000696
	" nitrate	0.000704	
Zinc^{Hg}	Zinc chloride (D.=1.05 to 1.06)	0.000696	0.000710
	Zinc sulphate	0.000696	
	" nitrate	0.000692	
	" acetate	0.000756	
Cadmium	Cadmium chloride	0.000615	0.000616
	" sulphate	0.000598	
	" nitrate	0.000634	
Mercury	Mercurous nitrate	0.000140	0.000140
Gold	Gold chloride	0.000024	0.000024

It will be observed that the numbers affixed to Zinc^{Hg} and copper are nearly the same, which, as stated elsewhere (see p. 198), accounts for the lack of variation in E. M. F. in the Daniell cell due to temperature changes. When the same metal forms two salifiable oxides, the values of the thermo-electric coefficient corresponding to each of them are different. The following results have been obtained with iron and iron salts :

Salt.	Thermo-electric coefficient. Daniell.	Average Daniell.
Ammoniacal sulphate of iron	— 0.000024	+ 0.000002
Ferrous sulphate	0.000000	
" chloride	+ 0.000077	
" acetate	+ 0.000087	
" tartrate	— 0.000127	
Ferric sulphate	— 0.00149	— 0.00156
Iron alum	— 0.00134	
Ferric nitrate	— 0.00169	
" chloride	— 0.00170	

The sign + indicates that it is the hot metal which is at the positive terminal; the sign — indicates the cold metal. A solution of ferrous chloride to which a small quantity of ferric chloride is added has given the following results :

Pure ferrous chloride........................... + 0.000077
Ferrous chloride with $\frac{1}{500}$ in volume of perchlo-
    ride solution................................. — 0.000284
Ferrous chloride with $\frac{1}{50}$ in volume of solution of
    perchloride................................. — 0.000599
Pure ferric chloride ...:........................ — 0.001700

Some other metals, such as silver, nickel, magnesium, aluminium, all more or less alterable in the solutions of their neutral salts, act like iron in salts of sesquioxide of iron ; that is to say, the hot metal is externally the negative pole.

With platinum electrodes Bouty obtained the following results (the figures are only approximate) :

Solution.	Thermo-electric Coefficient. Daniell.
Copper sulphate	— 0.000743
" nitrate	+ 0.001565
" chloride	+ 0.001485
Cadmium sulphate	+ 0.000139
" nitrate..................	+ 0.000382
" chloride	— 0.001013
Ferrous sulphate..................	— 0.000902
" chloride	— 0.000197
Ferric sulphate...................	+ 0.000986
" chloride....................	+ 0.000984
" nitrate....................	+ 0.001829
Nickel sulphate	+ 0.000456
" chloride	+ 0.000469
" nitrate	+ 0.000543

By multiplying the thermo-electric coefficient by 273 the E. M. F. of a couple having one surface at 0° absolute and the

other at 0° centigrade is obtained. The figures thus deter-
mined are those of the order of magnitude of the E. M. F.'s
of contact found directly between a metal and a liquid at the
ordinary temperature.

Metal.	Liquid.	Average E. M. F. for $1°$ (between 10° and 30°). Daniell.	Average.
Silver	{ Silver nitrate { Silver-plating bath	— 0.000165 } — 0.000240 }	— 0.000202
Nickel	{ Nickel chloride { " nitrate { " sulphate	— 0.00208 } — 0.00234 } — 0.00200 ꞵ }	— 0.00214
Magnesium Aluminum	{ Values greater than the preceding, but very un- { certain.		

*Determinations of the Thermo-electric Power of Zinc-zinc
Sulphate and of Copper-copper Sulphate* (Carhart, 1891).—1.
With zinc in zinc sulphate Professor Carhart finds a current
from cold to hot through the cell, and the following E. M. F.'s
corresponding to temperature differences :

Temp. Diff., corrected. (Cent.)	Change in E. M. F. in Legal Volts.	E. M. F. per Degree Cent.
0.2	. . . . . .	. . . . . .
9.2	0.00660	0.00072
13.8	0.00911	0.00065 ?
18.4	0.01319	0.00072
27.2	0.02011	0.00074
37.0	0.02812	0.00076
46.7	0.03707	0.00079

The mean thermo-electric power for a temperature of
23°.85 C. is 0.00079.

2. With copper and copper sulphate the current has the
same direction as in the preceding case, the cold copper acting
like the zinc in the ordinary cell.

Temperature Difference, corrected.	Change in E. M. F. in Legal volts.	E. M. F. per Degree C.
0.2	. . . . . .	. . . . . .
4.5	0.00252	0.00056
9.0	0.00582	0.00065
15.7	0.00944	0.00060
20.9	0.01369	0.00066
31.4	0.02061	0.00066
37.7	0.02611	0.00069
43.9	0.03162	0.00072
48.6	0.03524	0.00073

The mean thermo-electric power for the copper-copper sulphate couple is therefore 0.00073 for the mean temperature of 25° C. The details of Professor Carhart's experiments and their application to the Daniell cell will be found in his " Primary Batteries" (Boston, 1891).

E. M. F. of Thermo-electric Couples composed of Two Saline Solutions (Wild, 1858).—1. The thermo-electric forces are proportional to the differences of temperature of the two surfaces of contact of the electrolytes. This proportionality is maintained up to 50° C.

2. No current is produced when a point of a homogeneous liquid column is warmed, even when the temperatures are distributed asymmetrically on the two sides of the warmer point. A current is also not produced when two parts of the same liquid at different temperatures are brought suddenly together.

3. Two solutions of the same salt unequally concentrated give a weak thermo-electric current, which goes from the more dilute to the more concentrated solution through the warmed surface of contact.

4. The thermo-electric force of two electrolytes appears to decrease as the diffusion of one solution in the other takes place.

5. Electrolytes which satisfy Volta's law give, when their contact surfaces are brought to different temperatures, thermo-electric currents which satisfy Becquerel's law.

6. Electrolytes which do not satisfy the law of Volta do not satisfy the law of Becquerel.

The following table gives the values of the principal thermo-electric forces measured by Wild. The unit adopted is $\frac{1}{1000}$ of the E. M. F. of a Daniell cell. The difference of temperatures of contact is assumed to be 100° C. The figures adjoining the names indicate the density of the solutions.

Argentan ⎫
Copper   ⎭ 1.108

Bismuth ⎫
Copper ⎭ 6.26

Bismuth ⎫
Antimony ⎭ 10.03

Copper sulphate solution (1.10) ⎫
Potassium "   "   (1.07) ⎭ 6.34

Zinc   ⎫
Solution of zinc sulphate (1.12) ⎭ 100.00

Solution of copper sulphate (1.10) ⎫
Dilute sulphuric acid   (1.05) ⎭ 26.70

E. M. F.'s of Liquid Combinations which give a Current without Elevation of Temperature.

Solution of copper sulphate (1.10) ⎫
"   " potassium "   (1.07) ⎭ 9.97

Nitric acid   (1.05) ⎫
Solution of copper sulphate (1.10) ⎭ 9.97

Solution of copper sulphate (1.10) ⎫
"   " zinc   "   (1.20) ⎭ 8.64

Dilute sulphuric acid   (1.05) ⎫
Solution of copper sulphate (1.10) ⎭ 8.64

A Phenomenon Analogous to that of Peltier.—M. Bouty finds that when copper or zinc sulphate is electrolyzed between two electrode thermometers (thermometers covered with copper or zinc) by means of a Bunsen cell, the negative

thermometer rises above and the positive thermometer falls below the temperature of the surrounding liquid. This last effect, somewhat weaker than the first, may be estimated at about $\frac{1}{30}$ degree if the direction of the current be suddenly reversed. The electrolyte may be perfectly neutral or notably acid, provided it be sufficiently concentrated, so that there is no decomposition of the water: the direction of the current is not modified.

There is therefore at the positive electrode where the metal dissolves a permanent source of heat ; at the negative electrode, where the metal is deposited, a source of cold, each appearing very nearly equal and proportional to the intensity of the current.

De la Rue has shown that in tubes containing highly rarefied gases, thermometers placed in the vicinity of the two electrodes indicate temperatures which during the first few minutes are very different, the temperature being higher at the negative electrode. It is to be observed, however, that the difference of temperatures at the electrodes decreases in time, and finally disappears. The same is true when the elastic force of the gas augments. In a tube containing atmospheric air, for example, the difference of temperatures in the vicinity of the two electrodes becomes nothing when the pressure rises to 0.020 m.

CHAPTER XIV.

LIGHT CELLS.

Production of Electricity by the Action of Light (E. Becquerel, 1840).—A box of blackened wood was constructed, divided into two compartments by a very thin membrane. Each compartment contained a platinum electrode.

When an alkaline solution was introduced into the chambers, it was found that the plate exposed to the rays of the sun became negatively electrified with reference to the liquid, and that the inverse took place with an acid solution. This disengagement of electricity was not due to the action of heat. In fact, no action was perceptible when the red, orange, yellow, and green rays only were used. The effect under blue and indigo rays was small, and the most marked action occurred when the violet rays were employed.

When the plates of platinum and gold are very clean and have been alternately warmed to a red heat and dipped many times in nitric acid, the electric action is much diminished.

Other metals than gold and platinum, and particularly the alterable metals, such as silver and brass, produce similar effects. The previous polarization of the plates, especially after having been plunged in water, having been into contact with the positive pole of the battery, may greatly increase the electric effect observed.

If bodies that are alterable by light, such as the chloride, bromide, iodide of silver, etc., be placed on the surface of the plates at the moment of the action of the luminous rays, an energetic current is observed.

According to Grove (1858), when platinum electrodes in

acidulated water are used, the light acts simply to augment the current resulting from the polarization of the platinum.

Grove, however, determined, as Becquerel had done before, that heat is not the cause of the phenomenon. In fact, on submitting the platinum plates, not to white light, but to rays which had traversed a blue, yellow, or green glass, it was found that the blue light produced the most considerable action.

Zaliwski (1866) considers that among the depolarizers the most powerful ones are those which are most easily affected by the action of light. A cell the carbon of which is previously impregnated with an ammoniacal solution of silver chloride, then dried and treated with nitric acid to remove the excess of ammonia, should furnish, even with pure water, remarkable intensity. No experiment, however, is given in support of this idea.

Electricity Developed by the Exposure to Light of Dark Violet Crystals of Weardale (*England*) *Fluor Spar.*—Hankel (1874) has observed that the centre of a crystalline face of this body presents, after an exposure of about one hour to light, a high negative tension. An exposure of the crystal to a temperature of 95°, continued for several hours, produces, on cooling, but very small positive tension. Experiments made by passing the light through colored glasses, water, a solution of alum or quinine sulphate, show that the chemical effects are much the most active.

Too strong concentration of light on the crystalline face destroys its sensibility. The effects observed are much more intense than those obtained on heating the crystal or by rubbing its surface with a brush. They are, moreover, of contrary sign.

Borgmann's Photo-electric Cell (1883).—This consists of a tube in U-form filled with dilute sulphuric acid. In each arm of the tube is immersed a plate of silver covered with iodine.

A luminous ray projected on one of these plates generates an electric current by reason of the reduction of silver iodide.

Saur's Photo-electric Cell.—In a glass vessel is placed a solution of water 100 parts, sea-salt 15 parts, copper sulphate

7 parts. The porous cup is filled with mercury. Two electrodes, one a platinum plate, the other a plate of silver sulphide, are placed, the first in the mercury, the second in the copper solution. On placing the cell in the light, an electric current is yielded.

The copper bichloride formed by the mixture of sodium chloride and copper sulphate attacks the mercury. The copper protochloride formed reduces the silver sulphide, but as this reduction takes place only under the influence of solar rays, hence the current.

A cell formed of the couple zinc^{Hg}, silver sulphide, in salt water, when exposed to the sun produces a very perceptible current.

Selenium Cells.—These have been investigated by Mr. Shelford Bidwell.

Selenium exists in two allotropic forms, the one vitreous, as structureless as glass, closely resembling black sealing-wax, and when in thin films is capable of transmitting ruby-colored light ; the other form is amorphous and exists as a red powder. If left for half an hour at a temperature of 200° Fah. it becomes black. The amorphous variety is a non-conductor ; the specific resistance of one specimen, which had been carefully annealed, has been found by Mr. Bidwell to be as high as 2500 megohms. When the annealing took place in contact with copper, the specific resistance fell to some 900,000 ohms. The diminution of the resistance of selenium cells during the so-called annealing process is considered to be due, not to the effect of annealing, but to the formation of a conducting selenide of copper throughout the mass of selenium, beginning at the copper electrode.

Mr. Bidwell's method of constructing selenium cells, Fig. 129, is as follows: A strip of mica a few centimetres in length has copper wire wound over it from end to end, the distances between adjacent coils being about one twentieth of an inch. The wire is wound in two parallel coils, the two coils being carefully prevented from touching each other at any point, and forming the positive and the negative electrode respectively.

The size of wire is No. 36 ; it makes 20 turns per inch.   Melted selenium is poured on to the strip, and pressed in between the wires.   The cell is then kept for some time at a temperature of about 217°, and the resistance is found to fall gradually to
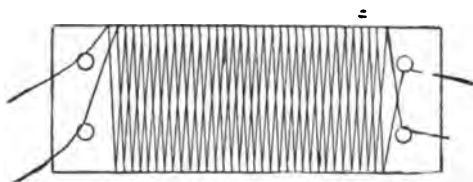
FIG. 129.—BIDWELL. SELENIUM CELL.

about 50,000 ohms.   The completed cell measures $2\frac{1}{4}$ inches by $\frac{3}{4}$ inch.

Professor W. G. Adams has found the resistance of selenium cells to fall in the course of a year to about one fortieth of their original value, this fall being in all probability due to the formation of selenide of copper.   Mr. Bidwell has observed the resistance of one of his cells to drop in the course of ten years from 80,000 ohms to 10 ohms. (Selenium cells show polarization effects, and develop an E. M. F. under the influence of light, forming photo-electric cells.   A selenium cell may be connected with a delicate relay and electric bell in such a manner that the diminution in the resistance of the cell on exposure to light will diminish the current through the relay and cause the bell to stop ringing.)

It is found that when different-colored plates of glass are interposed between the cell and the source of light—a gas-burner—red, orange, and yellow glasses exert no screening effect, but when a green glass is employed the light is cut off and the bell begins to ring.

(A light blue glass exerts a screening effect, while a much darker blue does not.   The reason of this, as shown by spectroscopic examination of the glasses, is that the dark blue glass, being colored with cobalt, allows a good deal of red light to traverse it, but the red light is entirely cut off by the light blue

glass. An arrangement of this kind may be employed to ring a bell in case of the extinction of a ship's light or of a railway signal light, or to turn on electric light when daylight falls below a certain point ; or apparatus arranged to ring a bell when the cell is exposed to light may be employed in a safe or strong-room, and made sufficiently delicate to be thrown into action by the lighting of a burglar's lantern.

The " selenium cell " is used in the photophone, by means of which sounds, and even articulate speech, can be transmitted from a distance. This is so contrived that, on speaking to the transmitting instrument, a beam of light reflected from it to the receiving station varies its intensity in exact accordance with the vibrations due to the voice. The beam falls on a selenium cell, which is in a circuit with a battery and a tele-phone. The resistance of the cell varies with the variations in the beam, and so also does the current. Hence the current at the receiving station varies in accordance with the vibrations due to the voice at the transmitting station, and the telephone thus reproduces the sounds uttered.

Minchin Photo-electric Impulsion Cell (1890).—This consists of a small glass tube, represented in Fig. 130, filled with either
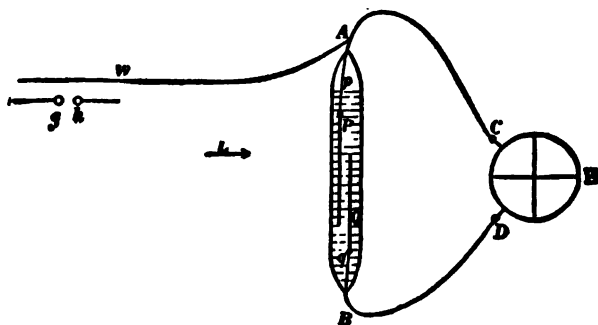
FIG. 130.—MINCHIN PHOTO-ELECTRIC IMPULSION CELL.

acetone or methylic alcohol ; two aluminium plates, P and Q, are immersed in the liquid; each plate is connected with a platinum wire. These wires pass through the ends of the

glass tube and are sealed into it. The terminals of the cell are *A B*, and these are connected with a quadrant electrometer.

The plate *P* is covered with a layer of sensitive selenium and is negative to the plate *Q*, which is quite clean—not sensitized to' light. The cell is fixed vertically in a clamp. When the cell is,of the " impulsion " kind, what happens is as follows: Daylight (represented by the arrow *L*) being allowed to fall on the sensitive plate *P*, the spot on the scale of the electrometer moves, and after a few seconds comes to rest, indicating an electromotive force varying with the intensity of the light.

On the withdrawal of the light, the deflection falls, and there are 'means of rapidly getting rid of the deflection without injury to the cell. Either before or after this deflection caused by light ceases, let a slight tap (sometimes inaudible) be given to the base or clamp in which the cell rests, and then results a remarkable change in the cell. It is no longer sensitive to light. This insensitive state is indicated by a rapid return motion of the spot on the scale; it is merely indicated by this motion, there being no necessary connection between this motion and the insensitive state, for if the cell were now left for some time (perhaps an hour or so) in the dark, the disturbing E. M. F. of the cell would vanish, and there would be nothing to tell us that the cell remains insensitive; but that it is really still in the insensitive state we find at once on again exposing it to light. Another gentle tap given to the clamp, or the stone table on which the whole apparatus rests, will restore the sensitive state ; and so on indefinitely, the sensitive and insensitive states following each other and being produced, in the case of many such cells, with great ease.

It is found that if a Voss machine, not in any way connected with the cell or the electrometer, was worked in the room while the cell was in the insensitive state, the moment a spark passed between the poles of the Voss, the insensitive state was altered to the sensitive, whether the cell was connected with the electrometer or not. The best method of showing the inductive effect of the spark is to connect an insulated wire *W*, apparently of any length, to either pole (*A* in

the figure) of the cell, and to place the poles *g h* of the Voss near the wire (a distance of several feet will do with a spark about half an inch long). If *g* and *h* are two or three feet from any part of the wire *W*, a spark about one eighth of an inch long suffices to change the cell from the insensitive to the sensitive state.

The sudden alteration of the insensitive to the sensitive state is produced in a most marked manner by the spark of a Hertz oscillator even at the distance of some thirty feet or more. The inventor considers that the results are due to the formation of some oscillating layer at the surface of the sensitive plate.

A pamphlet entitled *Das Phototel—Beitrage zum Problem des electrischen Fernsehens*, by R. E. Liesegang, published in Germany in 1892 (without date or place) contains a very complete résumé of past investigations in photo-electricity.

CHAPTER XV.

DRY CELLS AND EARTH AND SEA-WATER BATTERIES.

Two principal types of dry voltaic cell are recognized :

1. Those in which the electrodes are superposed after the manner of the voltaic pile, and in which moisture is obtained from the air, or from disks of cloth or like material soaked with the exciting liquid and interposed between the electrodes ; and

2. Those in which the exciting liquid is combined with some special absorbent, such as sawdust, etc., or made into a jelly.

A large number of dry cells have been devised, differing, however, only in the composition of the excitant, the ingredients of which are frequently kept secret. For uses which involve handling by unskilled persons they are convenient, and are best adapted to circumstances where current is intermittently needed and then only for a short time.

(1) DRY CELLS OF THE VOLTAIC-PILE TYPE.

The E. M. F. of these cells is quite high, but their resistance is considerable. Desormes and Hachette (1803) were the first who attempted to construct cells without conducting liquids and able to maintain themselves for a considerable period without loss of energy. Their battery consisted of a number of zinc-copper couples between which were interposed solid disks of starch paste mixed or not with salts, varnish, and various other substances. Biot (1804) also constructed a dry battery arranged similarly to the voltaic pile, except that the disks of cloth soaked in acidulated water were replaced by

disks of melted potassium nitrate. Dry batteries have been made with 20,000 pairs of disks, capable of charging a thin Leyden jar of 350 sq. cm. surface in ten minutes sufficiently to cause the discharge to melt 2.5 cm. of platinum wire 0.05 mm. in diameter.

Behrens Dry Battery.—Zinc-copper, gilded paper, successively.

Deluc Dry Battery (1809).—A large number of very thin disks of zinc and gilded paper superposed and pressed together by means of a screw.

Zamboni Dry Battery (1812).—Paper covered with tin on one face and binoxide of manganese on the other. About 200 elements are necessary for the decomposition of water. E. M. F. of each element = 0.2075 volt. The battery is constructed as follows: On the opposite sides of the sheets of tinned paper is applied a coating of olive oil, a solution of honey in considerable water, or better still a saturated solution of zinc sulphate. When this is barely dry, finely pulverized binoxide of manganese is applied. Several thousand sheets are superposed and pressed together. The exterior is covered with powdered sulphur.

Watkin Dry Battery (1828).—This consists of from sixty to eighty zinc plates cleaned and polished on one surface and not on the other. They are placed so that an air-space of 1 mm. thickness is left between them in a wooden trough. The E. M. F. is very low, resistance very high. Damp air favors the action.

All of the foregoing piles, in fact, depend for their action upon atmospheric moisture. If one be placed in a vessel in which the air is thoroughly dried by chloride of calcium, it yields no current.

Buff Dry Battery.—Numerous disks of gilded brass, zinc, and thin glass. Heat causes a weak current. A pile of ten couples produces a divergence of 10 mm. in the gold-leaf electroscope.

Shelford-Bidwell Dry Battery (1885).—The positive pole is a copper plate; the negative, a silver plate. Between the

plates is strongly compressed copper sulphide. E. M. F. $= 0.5$ volt; $R = 7$ ohms for an electrode surface of 61.55 by 50 mm. The intensity of the couple is 6800 microamperes through an external resistance of 0.2 ohm. The copper sulphide is decomposed into copper and sulphur. The copper is deposited on the copper plate, while the sulphur goes to the silver plate and is transformed into sulphide, so that in this arrangement the silver acts the part of the zinc in the ordinary cell. Mr. Bidwell finds that light diminishes while heat augments the current produced.

(2) DRY CELLS WITH ABSORBENTS.

Germain " Cofferdam" Dry Cell (1887).—In English naval practice the term "cofferdam" is applied to certain tight compartments formed on a ship by a double keel near and below the float water line. The name is also applied to the substances used for filling these compartments. Among such substances there is a preparation of cellulose made from the granular portion of the rind of the cocoanut. This material is in the form of a powder and has a density of 0.065. Before being used, it is compressed to a density of 0.133. This substance, which the French, following the English, call "cofferdam," has been applied by Mr. P. Germain in the construction of a form of the Leclanché cell that is easily transportable and can be turned in any direction, withstand blows, and be allowed to "fall from a height of five feet without interfering with the operation of the couple." Fig. 131 represents a longitudinal section of one of these cells. *A* is a light box made of wood boiled in paraffin and covered externally with cement. At the bottom (shown inverted in figure) of this box is arranged a bed, *B*, composed of a mixture of equal volumes of peroxide of manganese and granular carbon. Above this there is a plate, *C*, of agglomerated carbon of high conductivity, and then a second bed, *B*, like the first. The rest of the box is occupied by a layer, *D*, of "cofferdam" paste impregnated with a saturated solution of hydrochlorate of ammonia.

This paste is slightly compressed and then levelled, and its thickness is so regulated that it shall slightly exceed the level of the box. Finally, a strongly amalgamated plate of zinc (or rather a series of plates) rests upon the whole, and, exactly covering the cellulose, insulates the latter from the action of
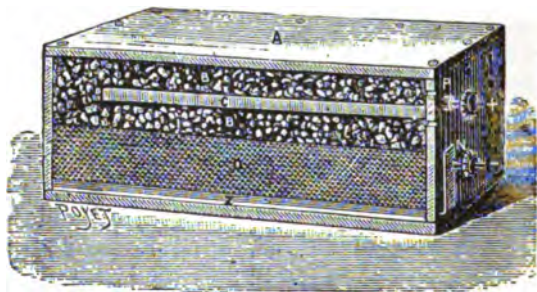
FIG. 131.—GERMAIN "COFFERDAM" DRY CELL.

the air. The inactive external surface of this electrode is protected from oxidation by a varnish made of bitumen. The pressure that it is necessary to exert upon the cellulose in order to fasten the lid down suffices at the same time to secure a liquid contact of the active surface of the electrodes with the paste. There are two apertures in one end of the box for the passage of the terminals, P and N. The positive terminal is connected with the carbon, and a threaded metallic rod, firmly cemented to the latter, permits of adapting to it a tightening button. The negative terminal is attached to a tail-piece cut in the external zinc plate. The peculiar arrangement of the zinc electrode is worthy of note. Instead of one thick plate, several distinct plates of the same size are used, each of which is amalgamated separately and then superposed one upon the other. The mercury is thus held between the plates. It is best to place the cell with the zinc downward. The electromotive force of this cell is 1.5 volts.

Cox Gelatine Dry Cell (1888).—The electrolyte consists of Irish or other sea moss boiled with sal-ammoniac to a uniform stiff pasty consistence. A small amount of bisulphate of mer-

cury is added which acidulates the electrolyte and keeps the zinc amalgamated.

Mehner Dry Cell (1889).—The exciting salts, consisting of suitable chlorides of the alkalies, are mixed with a "mineral gelatine," which consists of crystallized hydrated basic chloride of magnesium, which is formed by the addition of magnesia to a highly supersaturated and concentrated solution of magnesium chloride. If a suitable quantity of the solution of magnesium chloride is added to the oxide of magnesia, for example, in the first instance, a liquid product of a creamy consistency results, at first gradually gelatinizing and ultimately acquiring a pasty consistency. The degree of stiffness of the final product can be readily controlled by suitably regulating the addition of chloride solution. Dr. Mehner utilizes this property of oxychloride of magnesium in the preparation of his dry cell. The exciting salt is stirred with a solution of chloride of magnesium and calcined magnesia until a liquid of about the thickness of cream is obtained. This, after it is poured into the cell, becomes in a few days a thick pulp.

Nowotny Dry Cell (1890) has an outer vessel entirely of carbon, which is divided into two compartments by a carbon partition. The zinc is fork-shaped and straddles the partition. The space between zinc and carbon is packed, and the cell is hermetically sealed. E. M. F. claimed = 2 volts.

Oerlikon Dry Cell (1891).—Dilute sulphuric acid is mixed with the proper amount of a solution of silicate of soda or silicate of potassium and some asbestos fibre. This mixture, at first fluid, becomes stiff after a short time and is introdueed into the vessels containing the lead electrodes. A cell thus filled may "after several hours safely be reversed." This construction is applied to storage batteries.

Renault Dry Cell (1891) consists of a vessel made of retort-carbon in the bottom of which is a mixture of acid with gelatinous silica, which possesses the remarkable property of absorbing sixty times its volume of water. This mixture constitutes the active part of the cell. This part is isolated from the rest of the apparatus by a pipe-clay disk supporting a zinc

spiral, containing simple gelatinous silica in its convolutions. The action of the chromic acid is exerted upon the zinc in passing through the disk, and produces a current. The advantages of this battery reside in the wide extent of surface of the carbon vessel and of the zinc spiral, thus giving a maximum of surface along with a minimum of space. The cell is much the same in principle as the Leclanché, but the exciting fluid is contained in a paste, and the zinc electrode forms the containing vessel.

Gassner Dry Cell.—Two forms of the cell are made, one being cylindrical (Fig. 132), the other elliptical (Fig. 133). The

FIG. 132. GASSNER DRY CELL. FIG. 133.

carbon rod or plate occupies about one half of the space in the cell, and the space between the carbon and the cell is filled with the following mixture : " Oxide of zinc 1 part by weight, sal-ammoniac 1 part by weight, plaster 3 parts by weight, chloride of zinc 1 part by weight, water 2 parts by weight. The oxide of zinc in this composition loosens and makes it porous, and the greater porosity thus obtained facilitates the interchange of the gases and diminishes the tendency to the polarization of the electrodes." The mixture used in the cell differs somewhat with different manufacturers. E. M. F. about 1.3 volts.

Meserole's Composition for Dry Cells consists of charcoal 3 parts, mineral carbon or graphite 1 part, peroxide of manganese 3 parts, white arsenic oxide 1 part, a mixture of glucose and

dextrine or starch 1 part, and dry hydrate of lime 1 part,—all by weight. These ingredients are mixed and worked into a paste with a solution composed of equal parts of a saturated solution of ammonium chloride and common salt to which are added $\frac{1}{10}$ of the volume of a solution of mercury bichloride and an equal volume of hydrochloric acid.

Efficiency of Dry Cells.—Mr. J. A. Barrett in a paper in the *Electrical World*, Feb. 1890, states as follows :

" The office of water in primary batteries is twofold : first, it is to dissolve and hold in an operative state the chemicals by which the voltaic action of the cell is excited and continued ; and second, it is to dissolve and diffuse the chemical products resulting from that action. It is evident from this that the amount of water which any type of battery is capable of holding bears a direct relation to the amount of work which a fixed size of that particular battery is capable of yielding.

" The relations of these propositions to the 'dry' battery question will appear from an application to the case of zinc-carbon sal-ammoniac batteries. The amount of water which any cell will contain stands almost alone and nearly independent of the size and form of the electrodes as the limiting measure of the ultimate life of the battery at any work for which it is fitted. The size and form and quality of the electrodes affect the temporary constancy of the cell, but the question whether, in any specified service for which the cell is adapted, it will continue active for one month, or six months, or a year, is answered almost exclusively by the measured quantity of water which the cell is made to contain. In all these batteries it is the loss of sal-ammoniac and the accumulation of zinc oxides and ammonio-compounds which determines the final failure of battery action ; and consequently the displacement of the available water of solution in any degree by absorbent solids will proportionately shorten the active life of the cell. The impediment which the absorbent packing offers to the desirable diffusion and equalization of the soluble products in such cells is not referred to here, for, compared with the importance of the amount of water present for promoting the

solubility of these products, the free circulation of the fluid is only a secondary consideration.

"The value of an abundance of water in batteries will be still further emphasized by a statement of fact concerning the Leclanché battery. In this cell the serviceable life of the negative element is commonly supposed to be fixed by the amount of binoxide of manganese associated with the carbon conducting plate ; but it is susceptible of ready demonstration that long before the active oxygen of the manganese is exhausted, the element is declared used up and is customarily thrown out as worthless. The cause of this failure of the element is chiefly the accumulation in the porous cup and among the manganese of compounds of zinc which are insoluble in the scanty and impoverished fluid.

"The result of this condition is not so much a loss of electromotive force as an increase of internal resistance of the cell. Such a clogged-up element may be made fit for a renewed term of work by judicious treatment to a washing in dilute muriatic acid, and by setting up again with a fresh charge of sal-ammoniac; or the resuscitation may be partially secured without the washing by supplying the battery with a new and strong solution of sal-ammoniac, to which it is well to add a little muriatic acid.

"But the clogging up of the element and the period of its activity would have been in the first instance postponed if the element had been used in a larger jar with more water containing more sal-ammoniac. And conversely, the first life of the element would have been shortened by the employment of absorbent material and the consequent displacement of a part of the water of solution.

"A distinction should be recognized between the constancy of electromotive force under temporary test and the duration of the period over which the cell will perform a specified amount of work. The packing of the cell with inert matter to the exclusion of a portion of the water does not necessarily weaken its electromotive force, especially during the early stages of its service ; but by so much as the water is displaced,

the time is hastened when the original excitants of the battery lose their energy and are supplanted by the deleterious products of chemical action.

" What is here stated of zinc-carbon sal-ammoniac batteries is equally true of all types of cells in which the impoverishment of the battery in service is attributable to the accumulation of undissolved products. Those batteries in which chromic salts are employed will evidently do more and better work with a free fluid than if the chemicals are incompletely supplied with water. In fact, the principle is of pretty general application to all open-circuit batteries. On the basis of electrical measurement, therefore, it may be held that in efficiency and economy the fluid batteries are very considerably superior to the ' dry.' "

EARTH AND SEA-WATER BATTERIES.

Kemp` (1828) proposed placing in the sea, at a distance of half a mile apart, two large plates respectively of zinc and copper connected by an insulated wire along the shore. Shortly afterward Fox and Reich repeated this experiment with the plates buried in the earth. Becquerel, Magrini, Matteucci and others have also made investigations in the same direction. The various researches examined by Du Moncel have led to his formulating the following conclusions:

" 1. Oxidizable plates of the same metal and alike in size, connected by an insulated wire, may produce a quite energetic telluric current when they are buried in earth under different conditions of moisture. The current then passes through the wire from the plate in the soil which is the most damp— this plate acting like the electro-positive plate of a voltaic couple.

" 2. The current thus produced depends for its energy upon the extent of difference of humidity between the connected soils, on the attackability of the surface of the electro-positive plate, and on the size of the electro-negative plate.

" 3. The E. M. F. of current on a metallic circuit formed by

a telegraph wire of 3 mm. in diameter and 1735 metres in length may equal about one sixth that of the Daniell element.

"4. The current loses in strength as the soil around the plates becomes dry."

Palagi has obtained more powerful and more lasting effects by substituting a plate of carbon for the copper plate. Amalgamation of the zinc also increases the current intensity. A chain of 24 zincs was placed at the Oissel Bridge near Rouen, and one of forty carbons at Asnières, the intervening distance being 120 kilometres. The current operated a Wheatstone telegraph even with a single carbon. One of the most interesting observations made by Becquerel on these currents is that water is positive to earth when it comes from a stream or river, but negative when the water is stagnant, as at the bottom of a well. Lambron, who has studied the question with reference to thermal and sulphurous springs, finds, however, that under certain conditions Becquerel's conclusions must be modified. Thus the earth is always positive to sulphurous waters, whether the latter be running or stagnant. The phenomena noted by Becquerel most commonly occur with ordinary waters, but again according to Lambron the earth is negative to well-water from a sandy soil, and the water of such a well has the same polarity as that of the water-course. On the other hand, Lambron finds that this same running water may become negative to the earth after falling over rocks or when it is in a foamy or bubbling state.

Hogé and Pigott Earth Battery.—This consists of three plates of different metals of such a nature that one is electropositive and electro-negative to the other two respectively. These conditions are realized with copper, iron, and zinc. With this battery the current direction may be reversed. It is reported to have been used successfully on a telegraph line between Southampton and the Island of Guernsey. Du Moncel, however, states that the maximum distance over which such a telegraphic system can be worked is 20 kilometres.

Levoir Earth Battery.—According to Du Moncel, this consists in two plates, zinc and carbon, placed in porous vessels of

very large dimensions and buried in moist earth at the separated stations. The vessels each contain a different liquid. The liquid which surrounds the carbon electrode is water very slightly acidulated with nitric acid. The zinc is immersed in salt water. This battery has worked a telegraph line 57 kilometres long.

Pigott Submarine Battery.—By connecting the core of a cable with its iron envelope, an electric current has been obtained the intensity of which is equal to $\frac{1}{40000}$ part of that of the current furnished by a Daniell cell on a circuit of no resistance.

CHAPTER XVI.

GAS CELLS (Secondary Cells).

Gautherot (1801) appears to have been the first to observe that wires of platinum or silver after having been used for the decomposition of salt water possessèd the property of giving, after having been removed from the cell, an electric current opposite in direction and of short duration. Volta and Erman also observed that a piece of paper placed between two metallic plates serving as poles of a battery became itself polarized.

Ritter Cell (1803).—This consists of a series of gold plates superposed like the zinc-copper disks of the voltaic pile, and separated from one another by disks of cloth moistened with a saline solution. Ritter also used disks of platinum, copper, brass, iron, and bismuth, but he determined that the most energetic currents were given by gold, platinum, and silver.

Grove Cell (1829).—Hydrogenated platinum, oxygenated platinum. The platinum electrodes are immersed at their lower ends in dilute sulphuric acid (Fig. 134). Any voltameter containing water acidulated with sulphuric acid and platinum plates may serve as a gas cell. Grove's cell may work as a primary cell if the tubes of the voltameter be filled one with oxygen and the other with hydrogen prepared by ordinary chemical processes. According to Matteucci, the action of the platinum wires may be increased by warming them for a few moments in the flame of an alcohol lamp before using them as
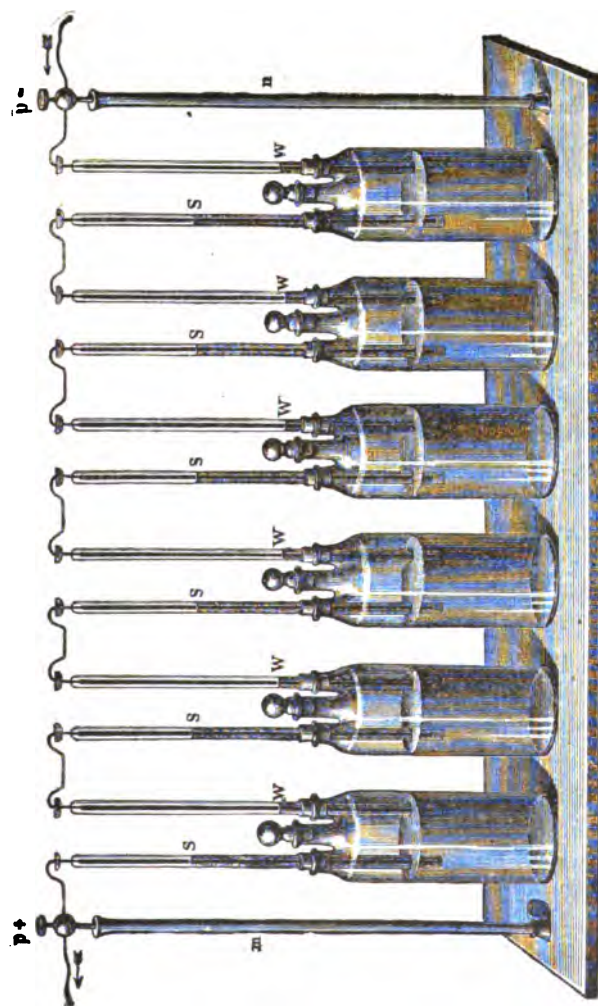
FIG. 134.—GROVE GAS BATTERY.

electrodes. Under the most favorable conditions the E. M. F. of the gas cell containing wires of non-platinized platinum scarcely exceeds 0.843 volt. The E. M. F. of the Grove element is independent of gas pressure; but its intensity (strength) is perceptibly proportional thereto.

Grove considered the seat of chemical action to be at the line of contact of the platinum liquid and gas. This appears inconsistent with the fact that a continuous current is obtained with water holding hydrogen in solution in one tube and oxygen in another. De la Rive (1843) and Gaugain (1867) thought the development of electricity in the Grove cell to be due to the chemical action exercised on the hydrogen, under the influence of the platinum, by the dissolved and not by the gaseous oxygen. According to H. F. Morley (1878), at least a part of the current from the gas cell is due to dissolved gas. Magunna (1886) concludes that the hydrogen which adheres to the platinum combines with the oxygen of the water, the hydrogen of which last forms an equal quantity of water with the oxygen surrounding the other platinum plate. There would be, therefore, at the positive electrode, decomposition and recomposition of a like amount of water; at the negative electrode, combination of the hydrogen of the water with the oxygen in the containing tube. Although the two gases may combine through the medium of the water, the conditions are as if the hydrogen contained in one tube combined directly with the oxygen contained in the other tube.

Gulcher Gas Cell.—This is constructed on the same principle as the Grove cell, with a special arrangement adapting it for practical use.

Smith Gas Cell.—A Grove gas cell so arranged as to accumulate gases under a pressure of 6 or 7 atmospheres, and to store it up in sufficient quantities so that the apparatus may act as an electrical reservoir.

A. S. Herschel Gas Cell (1882).—Platinum plates heated for several days at a high temperature in a crucible filled with lampblack. The surface of the plates has a rough carbon deposit. The cell is formed in the same way as the preceding.

Gaugain Gas Cells.—The simplest of these is that obtained by combining together under a high temperature glass tubes which contain respectively air and alcohol vapor. The nature of the electrodes, which act merely as conductors, is immaterial. Gaugain has experimented with the following couples:

> Air or oxygen and nitrogen;
> " " " " carbonic acid;
> " " " " hydrogen;
> " " " " water vapor;
> " " " " alcohol "
> " " " " ether "

The only active couples are those in which one of the elements is air or oxygen and the other an elastic fluid different from these two gases. The author considers that the current so generated is due to the action of oxygen on glass in a state of fusion, and that the second elastic fluid acts merely as a conductor. De la Rive, while recognizing the action of the oxygen upon the melted glass, holds that the phenomena observed by Gaugain are similar to those which take place in the Grove gas cell, with the difference that the electrolytic liquid which separates the two elastic fluids is melted glass instead of acidulated water.

E. Becquerel Gas Cell (1853).—Two platinum wires, one entirely immersed in a solution of gold chloride and the other immersed partly in gold chloride and partly in hydrogen. "The first wire takes positive electricity."

L. Maîche Gas Cell.—The current produced by this cell is obtained by oxidizing illuminating gas by atmospheric oxygen. The gas is led through a tube of rubber into a porous cup containing crushed carbon. Outside is platinized carbon exposed to the atmosphere. The liquid in the cell is acidulated water. When the circuit is closed, atmospheric oxygen combines with certain compounds of the gas, forming water. The current is very constant, but limited in production by the solubility of illuminating gas and oxygen in water.

Zenger Gas Cell (1883).—Carbon, gaseous bromine, carbon, hydrogen.

E. M. F. of Palladium in Gas Cells (*E. Villari*, 1870).— 1. If there be placed in hydrogen two electrodes, respectively of platinum and palladium, the palladium electrode is more oxidizable; and as the two metals are nearly of the same degree of inalterability in acidulated water, it follows that hydrogen is more oxidizable on contact with palladium than with platinum.

"The action of oxygen in gas cells with palladium electrodes is very complex and may materially affect experimental results. Platinum immersed in electrolytic oxygen, always containing ozone, acts energetically electropositive relatively to the same metal immersed in ordinary oxygen. In the case of palladium electrodes the action is still more complex, because, in addition to the formation of ozone by electro-chemical decomposition, the palladium which has operated as the positive electrode in a voltameter becomes coated with a dark red film of palladium oxide. This last dissolves rapidly in acidulated water, and in a short time the metal regains its lustre. It acts furthermore as a powerful oxidizer. On comparing two gas cells, one of which has platinum and the other palladium electrodes, the E. M. F. of the last is found to be the greater."

INFLUENCE OF THE E. M. F. OF A CELL ON THE POLARIZATION OF THE ELECTRODES. (E. BECQUEREL.)

Number of Cells.	E. M. F.'s		
	Of Cells Singly.	Of Cells over Voltameter.	Of the Voltameter.
1 Bunsen	1.666 volts	Barely 0.017 volts	....
2 "	3.270 "	0.773 "	2.497
3 "	5.084 "	2.307 "	2.777
4 "	6.825 "	4.522 "	2.303
6 "	10.200 "	6.987 "	3.113
8 "	13.381 "	10.115 "	3.266
10 "	16.711 "	13.319 "	3,392

The voltameter contained platinum electrodes and acidulated water. The figures of the fourth column, which are the differences between those of the second and third columns, give the effects of the secondary current due to the polarization of the voltameter plates by the oxygen and hydrogen. In simple couples it is necessary to consider only the inverse E. M. F. relative to the hydrogen, and there may be placed in the circuit an apparatus containing acidulated water and having for positive electrode a zinc plate and for negative electrode a plate of platinum. Experiment shows that the action of the simple couple is nearly constant and averages about 1.54 volts. Now, as the action exerted on the zinc alone by water acidulated with sulphuric acid is equal to 1.347 volts, it follows that polarization effect due to the hydrogen is 0.193 volt, or the difference between the above numbers (E. Becquerel).

Experiments to determine the part which each of the electrodes takes in polarization have so far yielded differing results. Poggendorff has found that both electrodes concur equally in the production of the developed E. M. F. Lenz and Saweljev, on the other hand, find that the cathode is more potent than the anode. According to Gaugain, the polarization of the anode remains always the same, but the polarization of the cathode increases when acidulated water is employed and attains the maximum with pure water. The following are the results obtained :

Distilled water $+ \frac{1}{10}$ } Polarization of the anode 10.0*
   sulphuric acid   }   "   ". cathode 8.1

                                    Total 18.1

Distilled water } Polarization of the anode 10.0
                  }   "   " cathode 12.5

                                      Total 22.5

* These numbers are merely simple ratios.

MAXIMUM E. M. F. OF A VOLTAMETER THE PLATINUM PLATES OF WHICH ARE SEPARATED BY A POROUS PARTITION.
(RAOULT, 1863.)

Water acidulated with sulphuric acid free from air. Current from five Bunsen cells :

	E. M. F.'s.
After 5 minutes' action...........	2.23 volts.
" 20 " "	2.27 "
" 1 day's "	2.32 "

With acidulated water, not boiled and without diaphragm:

After 5 minutes' action...........	2.13 volts.
" 20 " "	2.19 "
" 1 hour's "	2.23 "
" 1 day's "	2.11 "

Other observers find as maxima : Gaugain, 2.16 volts; Wheatstone, 2.34 volts; Lenz and Saweljev, 2.26 volts. It appears, therefore, that· the maximum E. M. F. of a voltameter containing acidulated water and platinum plates is nearly twice that of the Daniell element. These results do not agree with the E. M. F. (0.843 volt) generally assigned to the Grove gas cell. As Lenz and Saweljev have hitherto remarked, the E. M.F. of the Grove cell is the sum of the polarizations of the two electrodes, or

Polarization of the cathode	1.24 volts.
" " anode................	1.02 "
	2.26 "

Kohlrausch (1872) has found that in $\frac{1}{880000}$ of a second a current of 1 coulomb produces on platinum electrodes of 1 mm.

square section and immersed in dilute sulphuric acid a polarization equal to 1.079 volts. Grove has also obtained a current by substituting for the hydrogen and oxygen in his cell the following: chlorine and hydrogen; chlorine and oxygen; hydrogen and carbonic oxide; oxygen and carbonic oxide; ethylene and oxygen. Of these combinations the greatest E. M. F. is produced by chlorine and hydrogen, and the least by ethylene and oxygen. No current is yielded by the combination of nitrogen and oxygen, nitrogen and hydrogen, nitrogen protoxide and oxygen.

Grove has obtained a current with combinations of phosphorus and oxygen, and sulphur and oxygen. Each of these bodies was contained in one of the test-tubes of the gas cell: the tube enclosing the phosphorus or the sulphur, however, instead of containing air was filled with nitrogen, a gas completely indifferent in relation to oxygen. Sulphur produced no current unless liquefied by heat. A battery of ten phosphorus-oxygen cells decomposes water. In these experiments, as De la Rive has remarked, the phosphorus and sulphur vapors located in the inert nitrogen take the place of the hydrogen in the ordinary gas cell, and like it combine under the influence of the platinum, through the medium of the electrolytic liquid, with the oxygen contained in the opposite tube.

The Gas Battery as an Accumulator.—Mr. W. M. Stine has used for this purpose a modification of the Grove cell, and also a special form of carbon electrode. He states as follows: "The high absorptive power of finely-divided carbon for gases was utilized. Well-burned animal charcoal was treated with acid to dissolve out the mineral matter, and then thoroughly washed and dried at a high temperature to expel all gases absorbed by it This dried mass was moistened with a 40 per cent (by weight) solution of sulphuric acid and packed in small battery tumblers around the porous cups, which were also filled with the same mixture. Plain arc carbons were heated and inserted for the electrodes, and so connected as to make the carbon in the porous cup positive. A current of one

ampere was generally employed in charging, and the potential carefully noted by a voltmeter.

"A noticeable feature of these cells was the rapidity with which they acted with a very small charge. The first charge was continued for five minutes, and they behaved quietly and without gasing, except at the water-line if made too moist. Such charges usually developed voltages ranging from .9 to 1.4 volts. They were then discharged through an electric bell, to determine relative efficiency.

"The first five-minute charge given to a cell would usually ring the bell for nine minutes, and this increased by use to from 15 to 25 minutes. Increasing the time of charge showed that the cell reached its limit of economical capacity in about ten minutes, when the voltage became 1.7 to 1.9. When pushed beyond this the cells would gas badly, though the voltage increased slowly and in some cases reached 2.79 volts.

"The stability of the charge was, however, low. While standing charged for an hour the voltage decreased considerably, and the decrease was more marked during the first hour following the charge than subsequently. But the output in watts was but slightly lower than when discharged at once.

"The cells were frequently allowed to remain charged for 12 hours, and occasionally the charge had almost entirely disappeared by the end of this period. This was accounted for, in part, by the appearance of the oxygen, or positive electrode, when withdrawn from the cell; it was invariably eaten and furrowed. In one case where the cell had been in use for some time the electrode was found reduced to the thickness of a lead-pencil. It resembled the worn zinc from a Leclanché cell, and the carbon appeared to have been consumed rather than simply disintegrated. The hydrogen or negative electrode in no case showed signs of corrosion, except where, by change of polarity, it had been positive. This oxidation of the carbon finally led to an abandonment of the experiments.

"Though convinced that a gas battery, pure and simple, is not practicable, yet the idea of combining it with an accumu-

lator is an excellent one and should be successful. If, instead of combining the gas battery and the accumulator in a single cell, the gases were led through pipes into another cell, where they could be kept separated, this gas cell could be connected in parallel with the accumulator, and the energy lost by gasing almost completely restored. Were the gas cell to contain some absorbent substance in connection with a liquid, it would appear to yield better results."

CHAPTER XVII.

GENERAL PRACTICAL DATA.

CLASSIFICATION OF METALS WITH REFERENCE TO THEIR ELECTROMOTIVE FORCES.

IN the following lists each metal is positive in the cell in relation to all which follow and negative in relation to all which precede it when immersed in the exciting liquids stated. The original classification by Volta is as follows: Zinc, lead, tin, iron, copper, silver, gold, carbon, graphite, manganese.

DISTILLED WATER (Matthiessen and Bunsen).—Potassium, sodium, lithium, calcium, strontium, magnesium.

WATER (Fechner).—Zinc, lead, tin, iron, antimony, bismuth, copper, silver, gold.

DILUTE ACIDS (Davy).—Potassium, barium, amalgamated zinc, zinc, ammonium amalgam, cadmium, tin, iron, antimony, lead, copper, silver, palladium, tellurium, gold, platinum, iridium, rhodium.

SULPHURIC ACID 1 PART + WATER 1 PART (Pfaff).—Zinc, cadmium, tin, lead, tungsten, iron, bismuth, antimony, copper, silver, gold, tellurium, platinum, palladium.

VERY DILUTE SULPHURIC ACID (Marianini).—Zinc, carbon heated and cooled, lead, tin, manganese, iron, loadstone, bronze, copper, oxidized bronze, bismuth, nickel, carbon, antimony, natural sulphide of molybdenum, arsenic, silver, mercury, galena, arsenical cobalt, black tellurium, cupreous pyrites, gold, native auriferous tellurium, cubical iron pyrites, graphite, peroxide of manganese.

HYDROCHLORIC ACID (Faraday).—Zinc, cadmium, tin, lead, iron, copper, bismuth, nickel, silver, antimony.

NITRIC ACID 1 VOL., WATER 7 VOLS. (Faraday).—Zinc, cadmium, lead, tin, iron, nickel, bismuth, antimony, copper, silver.

NITRIC ACID, D. = 1.48 (Faraday).—Cadmium, zinc, lead, tin, iron, bismuth, copper, antimony, silver, nickel.

CONCENTRATED NITRIC ACID (De la Rive).—Tin, zinc, iron, copper, lead, mercury, silver, lead peroxide.

10% SOLUTION OF PURE HYDROFLUORIC ACID (G. Gore). —Aluminium, zinc, magnesium, thallium, cadmium, tin, lead, silicium, iron, nickel, cobalt, antimony, bismuth, copper, silver, gold, retort-carbon, platinum.

28% SOLUTION OF PURE HYDROFLUORIC ACID (G. Gore). —Zinc, magnesium, aluminium, thallium, indium, cadmium, tin, lead, silicium, iron, nickel, cobalt, antimony, bismuth, mercury, silver, gold, arsenic, osmium, ruthenium, retort-carbon, platinum, rhodium, palladium, tellurium, osmiridium, gold, iridium.

ANHYDROUS HYDROFLUORIC ACID, T. = − 17°.7 (G. Gore).—Zinc, tin, lead, cadmium, indium, magnesium, cobalt, aluminium, iron, nickel, bismuth, thallium, copper, indium, silver, retort-carbon, gold, platinum, palladium.

SOLUTION OF POTASH OR SODA (H. Davy).—Alkaline metals, zinc, tin, lead, copper, iron, silver, palladium, gold, platinum.

SOLUTION OF POTASH OR SODA, CONCENTRATED OR DI-LUTED (Faraday).—Zinc, tin, cadmium, antimony, lead, bismuth, iron, copper, nickel, silver.

SOLUTION OF POTASH OR SODA, D. = 1.33 (Pfaff).—Tin, zinc, antimony, lead, copper, gold, platinum, bismuth, steel, silver.

SOLUTION OF POTASH (A. Bennett, 1875).—Zinc, lead, tin, arsenic, copper, cobalt, nickel, soft iron, steel, gold, platinum, carbon, silver.

SOLUTION OF AMMONIA, D. = 0.95 (Pfaff).—Zinc, tin, lead, silver, copper.

SOLUTION OF AMMONIUM CHLORIDE (Poggendorff).—Zinc, cadmium, manganese, lead, tin, iron, steel, uranium, brass, magnetic iron, maillechort, cobalt, bismuth, antimony, arsenic, chromium, silver, mercury, copper, pyrites, tellurium, gold, galena, coke, platinum, plumbago, manganese peroxide.

SOLUTION OF SODIUM CHLORIDE (Fechner).—Zinc, lead, tin, iron, antimony, bismuth, copper, silver, gold, platinum.

1 PART POTASSIUM CYANIDE IN 8 PARTS OF WATER (Poggendorff).—Amalgamated zinc, zinc, copper, cadmium, tin, silver, nickel, antimony, lead, mercury, palladium, bismuth, wrought-iron, platinum, cast-iron, coke.

1 PART POTASSIUM FERROCYANIDE AND 8 PARTS OF WATER (Poggendorff).—Zinc, cadmium, lead, copper, antimony, tin, bismuth, nickel, cast-iron, wrought-iron, palladium, silver, carbon, platinum.

DILUTE SOLUTION OF POTASSIUM SULPHYDRATE (H. Davy).—Zinc, tin, copper, iron, bismuth, silver, platinum, palladium, gold, carbon.

YELLOW SOLUTION OF POTASSIUM SULPHATE (Faraday).—Cadmium, zinc, copper, tin, antimony, silver, lead, bismuth, nickel, iron.

DILUTE SOLUTION OF PENTASULPHIDE OF POTASSIUM (Faraday).—Zinc, copper, cadmium, tin, silver, lead, antimony, nickel, bismuth, iron.

DILUTE SOLUTION OF FLUORIDE OF SILVER (G. Gore).—Aluminium, magnesium, silicium, iridium, rhodium, wood-carbon (*lignum vitæ*), platinum, silver, palladium, tellurium, gold.

FUSED BORIC ACID (G. Gore).—Iron, silicium, carbon, platinum, gold, copper, silver.

FUSED PHOSPHORIC ACID (G. Gore).—Zinc, iron, copper, silver, platinum.

FUSED POTASSIUM HYDRATE (G. Gore).—Silicium, aluminium, zinc, iron, lead, carbon, platinum, silver.

FUSED POTASSIUM CARBONATE (G. Gore).—Silicium, iron, zinc, carbon, copper, silver, platinum.

FUSED POTASSIUM CHLORIDE (G. Gore).—Aluminium, zinc, iron, copper, silver, platinum.

FUSED POTASSIUM FLUORIDE (G. Gore).—Palladium, gold, platinum, iridium.

FUSED SILVER FLUORIDE (G. Gore).—Silver, platinum, wood-carbon (*lignum vitæ*), palladium, gold.

FUSED AMMONIUM NITRATE (G. Gore).—Magnesium, zinc, lead, copper, silver, tin, aluminium, iron, silicium, carbon, platinum.

In the following tables are given the similar classifications of metals, etc., in different solutions carried to different degrees of concentration and also maintained at different temperatures.

<div align="right">TABLE</div>

SOLUTIONS OF CHLORIDE OF POTASSIUM AT DIFFERENT

<div align="right">(G. GORE,</div>

Quantity of ClK.	0.139%	0.324%	1.296%	2.592%	5.184%
	Magnesium	Magnesium	Magnesium	Magnesium	Magnesium
	Zinc	Zinc	Zinc	Zinc	Zinc
	Cadmium	Thallium	Cadmium	Aluminium	Cadmium
	Thallium	Aluminium	Thallium	Cadmium	Aluminium
	Aluminium	Cadmium	Aluminium	Thallium	Thallium
	Indium	Indium	Indium	Indium	Indium
	Tin	Lead	Iron	Lead	Lead
	Lead	Iron	Lead	Iron	Tin
	Silicium	Tin	Tin	Tin	Iron
	Iron	Cobalt	Silicium	Silicium	Cobalt
	Cobalt	Silicium	Cobalt	Cobalt	Silicium
	Copper	Antimony	Nickel	Antimony	Antimony
	Antimony	Bismuth	Copper	Copper	Bismuth
	Bismuth	Copper	Antimony	Nickel	Copper
	Mercury	Nickel	Bismuth	Bismuth	Nickel
	Nickel	Tellurium	Tellurium	Tellurium	Tellurium
	Tellurium	Iridium	Mercury	Silver	Mercury
	Iridium	Mercury	Palladium	Palladium	Gold
	Rhodium	Rhodium	Silver	Mercury	Silver
	Palladium	Palladium	Gold	Gold	Palladium
	Gold	Gold	Iridium	Platinum	Iridium
	Silver	Silver	Platinum	Iridium	Platinum
	Platinum	Platinum	Rhodium	Rhodium	Rhodium
	Carbon	Carbon	Carbon	Carbon	Carbon

<div align="right">TABLE</div>

SOLUTIONS OF CHLORIDE OF POTASSIUM AT DIFFERENT

<div align="right">(G. GORE,</div>

Quantity of ClK.	0.139%	0.324%	1.296%	2.592%	5.184%
	Magnesium	Magnesium	Magnesium	Magnesium	Magnesium
	Zinc	Zinc	Zinc	Zinc	Zinc
	Thallium	Thallium	Thallium	Thallium	Cadmium
	Aluminium	Aluminium	Cadmium	Aluminium	Aluminium
	Cadmium	Cadmium	Aluminium	Cadmium	Thallium
	Indium	Indium	Indium	Indium	Indium
	Lead	Lead	Lead	Lead	Lead
	Tin	Iron	Iron	Iron	Iron
	Iron	Tin	Tin	Tin	Tin
	Silicium	Cobalt	Cobalt	Cobalt	Cobalt
	Cobalt	Silicium	Silicium	Silicium	Antimony
	Antimony	Antimony	Antimony	Antimony	Bismuth
	Bismuth	Bismuth	Nickel	Bismuth	Silicium
	Copper	Copper	Bismuth	Copper	Copper
	Mercury	Nickel	Copper	Nickel	Nickel
	Nickel	Tellurium	Tellurium	Tellurium	Tellurium
	Tellurium	Iridium	Silver	Silver	Silver
	Iridium	Mercury	Palladium	Mercury	Mercury
	Rhodium	Rhodium	Mercury	Iridium	Iridium
	Palladium	Palladium	Gold	Rhodium	Rhodium
	Gold	Gold	Iridium	Palladium	Gold
	Silver	Silver	Rhodium	Gold	Palladium
	Platinum	Platinum	Platinum	Platinum	Platinum
	Carbon	Carbon	Carbon	Carbon	Carbon

I.

DEGREES OF CONCENTRATION. TEMPERATURE = 12°.78 C.

1879.)

10.37%	15.55%	20.73%	25.92%	31.10%	Saturated.
Magnesium	Magnesium	Magnesium	Magnesium	Magnesium	Magnesium
Zinc	Zinc	Zinc	Zinc	Zinc	Zinc
Cadmium	Cadmium	Cadmium	Cadmium	Cadmium	Cadmium
Aluminium	Aluminium	Aluminium	Aluminium	Aluminium	Aluminium
Thallium	Thallium	Thallium	Thallium	Thallium	Thallium
Indium	Indium	Indium	Indium	Indium	Indium
Lead	Lead	Lead	Lead	Lead	Lead
Tin	Tin	Tin	Tin	Tin	Tin
Iron	Iron	Iron	Iron	Iron	Iron
Cobalt	Cobalt	Cobalt	Cobalt	Cobalt	Cobalt
Silicium	Silicium	Antimony	Silicium	Silicium	Copper
Antimony	Antimony	Copper	Antimony	Antimony	Antimony
Copper	Copper	Nickel	Copper	Copper	Bismuth
Bismuth	Bismuth	Silicium	Nickel	Bismuth	Silicium
Nickel	Nickel	Bismuth	Bismuth	Nickel	Nickel
Tellurium	Tellurium	Tellurium	Tellurium	Silver	Silver
Silver	Silver	Silver	Silver	Tellurium	Tellurium
Mercury	Iridium	Mercury	Mercury	Mercury	Mercury
Palladium	Mercury	Iridium	Iridium	Iridium	Iridium
Iridium	Gold	Gold	Gold	Gold	Palladium
Gold	Palladium	Palladium	Palladium	Palladium	Gold
Platinum	Platinum	Platinum	Platinum	Platinum	Rhodium
Rhodium	Rhodium	Rhodium	Rhodium	Rhodium	Platinum
Carbon	Carbon	Carbon	Carbon	Carbon	Carbon

II.

DEGREES OF CONCENTRATION. TEMPERATURE = 37°.78 C.

1879.)

10.37%	15.55%	20.73%	25.92%	31.10%	Saturated.
Magnesium	Magnesium	Magnesium	Magnesium	Magnesium	Magnesium
Zinc	Zinc	Zinc	Zinc	Zinc	Zinc
Cadmium	Cadmium	Cadmium	Cadmium	Cadmium	Cadmium
Aluminium	Aluminium	Aluminium	Aluminium	Aluminium	Aluminium
Thallium	Thallium	Thallium	Thallium	Thallium	Thallium
Indium	Indium	Indium	Indium	Indium	Indium
Lead	Lead	Lead	Lead	Lead	Lead
Iron	Iron	Iron	Tin	Tin	Tin
Tin	Tin	Tin	Iron	Iron	Iron
Cobalt	Cobalt	Cobalt	Cobalt	Cobalt	Cobalt
Silicium	Silicium	Antimony	Antimony	Antimony	Antimony
Antimony	Antimony	Silicium	Copper	Antimony	Copper
Copper	Copper	Copper	Bismuth	Copper	Bismuth
Bismuth	Bismuth	Bismuth	Silicium	Bismuth	Silicium
Nickel	Nickel	Nickel	Nickel	Silicium	Nickel
Tellurium	Tellurium	Tellurium	Tellurium	Nickel	Silver
Silver	Silver	Silver	Silver	Silver	Tellurium
Iridium	Iridium	Mercury	Mercury	Tellurium	Mercury
Mercury	Mercury	Iridium	Iridium	Mercury	Iridium
Palladium	Palladium	Gold	Gold	Iridium	Gold
Gold	Rhodium	Palladium	Palladium	Gold	Palladium
Platinum	Gold	Platinum	Platinum	Palladium	Platinum
Rhodium	Platinum	Rhodium	Rhodium	Rhodium	Rhodium
Carbon	Carbon	Carbon	Carbon	Platinum	Carbon

THE VOLTAIC CELL.

Quantity of BrK.	0.139 %	0.324%	1.296%	2.592%	5.184%	10.37%	15.55%
	Magnesium	Magnesium	Magnesium	Magnesium	Magnesium	Magnesium	Magnesium
	Zinc	Zinc	Zinc	Zinc	Zinc	Zinc	Zinc
	Thallium	Thallium	Thallium	Cadmium	Cadmium	Cadmium	Cadmium
	Cadmium	Cadmium	Cadmium	Thallium	Thallium	Thallium	Thallium
	Indium	Indium	Indium	Indium	Indium	Indium	Aluminium
	Aluminium	Aluminium	Aluminium	Aluminium	Aluminium	Aluminium	Indium
	Iron	Iron	Iron	Iron	Lead	Lead	Lead
	Lead	Lead	Lead	Lead	Iron	Iron	Iron
	Tin	Tin	Tin	Tin	Tin	Tin	Tin
	Cobalt	Cobalt	Cobalt	Cobalt	Cobalt	Cobalt	Cobalt
	Antimony	Antimony	Antimony	Antimony	Antimony	Antimony	Antimony
	Silicium	Silicium	Silicium	Silicium	Silicium	Silicium	Copper
	Bismuth	Bismuth	Bismuth	Bismuth	Bismuth	Bismuth	Silicium
	Nickel	Nickel	Copper	Copper	Copper	Copper	Bismuth
	Tellurium	Copper	Nickel	Nickel	Nickel	Nickel	Nickel
	Copper	Tellurium	Silver	Silver	Silver	Silver	Silver
	Mercury	Mercury	Mercury	Mercury	Mercury	Mercury	Mercury
	Silver	Silver	Tellurium	Tellurium	Tellurium	Tellurium	Tellurium
	Palladium	Palladium	Palladium	Palladium	Palladium	Palladium	Palladium
	Iridium	Iridium	Iridium	Iridium	Iridium	Iridium	Iridium
	Rhodium	Gold	Gold	Gold	Gold	Gold	Gold
	Gold	Rhodium	Rhodium	Rhodium	Platinum	Rhodium	Platinum
	Platinum	Platinum	Platinum	Platinum	Rhodium	Platinum	Rhodium
	Carbon	Carbon	Carbon	Carbon	Carbon	Carbon	Carbon

Quantity of BrK.	0.139%	0.324%	1.296%	2.592%	5.184%	10.37%	15.55%
	Magnesium	Magnesium	Magnesium	Magnesium	Magnesium	Magnesium	Magnesium
	Zinc	Zinc	Zinc	Zinc	Zinc	Zinc	Zinc
	Thallium	Thallium	Thallium	Thallium	Cadmium	Cadmium	Cadmium
	Cadmium	Cadmium	Cadmium	Cadmium	Thallium	Thallium	Thallium
	Indium	.ndium	Indium	Indium	Indium	Indium	Aluminium
	Aluminium	Aluminium	Aluminium	Aluminium	Aluminium	Aluminium	Indium
	Lead	Lead	lron	Antimony	Lead	Lead	Lead
	Tin	Iron	Lead	Iron	Iron	Iron	Tin
	Iron	Tin	Tin	Tin	Tin	Tin	Iron
	Cobalt	Cobalt	Cobalt	Cobalt	Cobalt	Cobalt	Cobalt
	Antimony	Antimony	Antimony	Antimony	Antimony	Antimony	Antimony
	Silicium	Silicium	Silicium	Silicium	Silicium	Silicium	Copper
	Bismuth	Bismuth	Bismuth	Bismuth	Bismuth	Copper	Silicium
	Nickel	Nickel	Copper	Copper	Copper	Bismuth	Bismuth
	Tellurium	Copper	Nickel	Nickel	Nickel	Nickel	Nickel
	Copper	Tellurium	Silver	Silver	Silver	Silver	Silver
	Silver	Mercury	Mercury	Mercury	Mercury	Mercury	Mercury
	Mercury	Silver	Tellurium	Tellurium	Tellurium	Tellurium	Tellurium
	Iridium	Palladium	Palladium	Palladium	Palladium	Palladium	Palladium
	Palladium	Iridium	Iridium	Iridium	Iridium	Gold	Iridium
	Rhodium	Gold	Gold	Gold	Gold	Iridium	Gold
	Gold	Rhodium	Platinum	Rhodium	Platinum	Rhodium	Rhodium
	Platinum	Platinum	Rhodium	Platinum	Rhodium	Platinum	Platinum
	Carbon	Carbon	Carbon	Carbon	Carbon	Carbon	Carbon

III.

DEGREES OF CONCENTRATION. TEMPERATURE = 12°.78 C.

1879.)

20.73%	25.92%	31.10%	36.28%	41.47%	46.65%	Saturated.
Magnesium	Magnesium	Magnesium	Magnesium	Magnesium	Magnesium	Magnesium
Zinc	Zinc	Zinc	Zinc	Zinc	Zinc	Zinc
Cadmium	Cadmium	Cadmium	Cadmium	Cadmium	Cadmium	Cadmium
Thallium	Thallium	Thallium	Thallium	Thallium	Thallium	Thallium
Aluminium	Aluminium	Aluminium	Aluminium	Aluminium	Aluminium	Aluminium
Indium	Indium	Indium	Indium	Indium	Indium	Lead
Lead	Lead	Lead	Lead	Lead	Lead	Indium
Iron	Tin	Tin	Tin	Tin	Tin	Tin
Tin	Iron	Iron	Iron	Iron	Iron	Iron
Cobalt	Cobalt	Cobalt	Cobalt	Copper	Copper	Copper
Copper	Copper	Copper	Copper	Cobalt	Cobalt	Cobalt
Antimony	Antimony	Antimony	Antimony	Antimony	Antimony	Antimony
Silicium	Silicium	Silicium	Silicium	Silicium	Silicium	Silicium
Bismuth	Bismuth	Bismuth	Bismuth	Bismuth	Bismuth	Bismuth
Nickel	Nickel	Silver	Silver	Silver	Silver	Silver
Silver	Silver	Nickel	Nickel	Nickel	Nickel	Nickel
Mercury	Mercury	Mercury	Mercury	Mercury	Mercury	Mercury
Tellurium	Tellurium	Tellurium	Tellurium	Palladium	Palladium	Palladium
Palladium	Palladium	Palladium	Palladium	Tellurium	Gold	Gold
Iridium	Iridium	Gold	Gold	Gold	Tellurium	Tellurium
Gold	Gold	Platinum	Platinum	Platinum	Platinum	Platinum
Platinum	Platinum	Iridium	Iridium	Iridium	Iridium	Iridium
Rhodium	Rhodium	Rhodium	Rhodium	Rhodium	Rhodium	Rhodium
Carbon	Carbon	Carbon	Carbon	Carbon	Carbon	Carbon

IV.

DEGREES OF CONCENTRATION. TEMPERATURE = 37°.78 C.

1879.)

20.73%	25.92%	31.10%	36.28%	41.47%	46.65%	Saturated.
Magnesium	Magnesium	Magnesium	Magnesium	Magnesium	Magnesium	Magnesium
Zinc	Zinc	Zinc	Zinc	Zinc	Zinc	Zinc
Cadmium	Cadmium	Cadmium	Cadmium	Cadmium	Cadmium	Cadmium
Thallium	Thallium	Thallium	Thallium	Thallium	Thallium	Thallium
Aluminium	Aluminium	Aluminium	Aluminium	Aluminium	Aluminium	Aluminium
Indium	Indium	Indium	Indium	Indium	Indium	Indium
Lead	Lead	Lead	Lead	Lead	Lead	Lead
Tin	Tin	Tin	Tin	Tin	Tin	Tin
Iron	Iron	Iron	Iron	Iron	Iron	Iron
Cobalt	Cobalt	Cobalt	Cobalt	Copper	Copper	Cobalt
Copper	Copper	Copper	Copper	Cobalt	Cobalt	Copper
Antimony	Antimony	Antimony	Antimony	Antimony	Antimony	Antimony
Silicium	Silicium	Silicium	Silicium	Silicium	Silicium	Silicium
Bismuth	Bismuth	Bismuth	Bismuth	Silver	Bismuth	Silver
Nickel	Nickel	Silver	Silver	Bismuth	Silver	Bismuth
Silver	Silver	Nickel	Nickel	Nickel	Nickel	Nickel
Mercury	Mercury	Mercury	Mercury	Mercury	Mercury	Mercury
Tellurium	Tellurium	Tellurium	Tellurium	Palladium	Palladium	Palladium
Palladium	Palladium	Palladium	Palladium	Tellurium	Gold	Gold
Iridium	Gold	Gold	Gold	Gold	Tellurium	Tellurium
Gold	Platinum	Platinum	Iridium	Platinum	Platinum	Platinum
Platinum	Iridium	Iridium	Platinum	Iridium	Iridium	Iridium
Rhodium	Rhodium	Rhodium	Rhodium	Rhodium	Rhodium	Rhodium
Carbon	Carbon	Carbon	Carbon	Carbon	Carbon	Carbon

SOLUTIONS OF IODIDE OF POTASSIUM AT DIFFERENT

(G. GORE,

Quan-tity of IK.	0.139%	0 324%	1.296%	2.592%	5.184%	10.37%	15.55%	20.73%	25.92%
	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg
	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn
	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd
	Ga	Ga	Ga	Ga	Ga	Ga	Ga	Ga	Ga
	Tl	Tl	Tl	Tl	Tl	Tl	Tl	Tl	Tl
	Al	Al	Al	Al	Al	Al	Al	Al	Al
	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb
	Sn	Sn	Sn	Sn	Sn	Sn	Sn	Sn	Sn
	In	In	In	In	In	In	In	In	In
	Fe	Fe	Fe	Fe	Fe	Fe	Fe	Fe	Fe
	Co	Co	Co	Co	Co	Co	Cu	Cu	Cu
	Sb	Sb	Cu	Cu	Cu	Cu	Co	Ag	Sb
	Cu	Cu	Sb	Sb	Sb	Sb	Sb	Co	Ag
	Si	Si	Si	Si	Ag	Ag	Ag	Sb	Co
	Bi	Bi	Ag	Ag	Si	Hg	Hg	Hg	Hg
	Ni	Ag	Bi	Hg	Hg	Si	Si	Si	Bi
	Ag	Ni	Ni	Bi	Bi	Bi	Bi	Bi	Si
	Hg	Hg	Hg	Ni	Ni	Ni	Ni	Ni	Ni
	Pd	Pd	Pd	Pd	Pd	Pd	Pd	Pd	Pd
	Au	Au	Te	Au	Au	Au	Te	Te	Au
	Te	Te	Au	Te	Te	Te	Au	Au	Te
	Pt	Pt	Pt	Pt	Pt	Pt	Pt	Pt	Pt
	Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir
	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh
	C	C	C	C	C	C	C	C	C

V.

DEGREES OF CONCENTRATION. TEMPERATURE = 15°.56 C.
1879.)

31.10%	36.28%	41.47%	46.65%	51.84%	64.80%	77.76%	103.6%	179.6%	Satu-rated.
Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg
Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn
Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd
Ga	Ga	Ga	Ga	Ga	Ga	Ga	Ga	Ga	Ga
Tl	Tl	Tl	Tl	Tl	Tl	Tl	Tl	Tl	Tl
Al	Al	Al	Al	Al	Al	Al	Al	Al	Al
Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb
Sn	Sn	Sn	Sn	Sn	Sn	Sn	Sn	Sn	Sn
In	In	In	In	In	In	In	In	In	In
Fe	Fe	Fe	Fe	Fe	Cu	Cu	Cu	Cu	Cu
Cu	Cu	Cu	Cu	Cu	Ag	Ag	Ag	Ag	Ag
Co	Ag	Ag	Ag	Ag	Fe	Fe	Hg	Hg	Sb
Sb	Co	Sb	Sb	Sb	Sb	Sb	Fe	Sb	Fe
Ag	Sb	Co	Co	Hg	Hg	Hg	Sb	Fe	Hg
Hg	Hg	Hg	Hg	Co	Co	Co	Bi	Co	Co
Bi	Bi	Bi	Bi	Bi	Bi	Bi	Co	Bi	Bi
Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
Ni	Ni	Ni	Ni	Ni	Ni	Ni	Ni	Ni	Ni
Pd	Pd	Pd	Pd	Pd	Pd	Pd	Au	Pd	Pd
Au	Au	Au	Au	Au	Au	Au	Pd	Te	Te
Pt	Te	Pt	Te	Te	Te	Pt	Te	Au	Au
Te	Pt	Te	Pt	Pt	Pt	Te	Pt	Pt	Pt
Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir
Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh
C	C	C	C	C	C	C	C	C	C

TABLE

SOLUTIONS OF IODIDE OF POTASSIUM AT DIFFERENT

(G. GORE,

Quantity of IK.	0.139%	0.324%	1.296%	2.592%	5.184%	10.37%	15.55%	20.73%	25.92%
	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg
	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn
	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd
	Tl	Tl	Tl	Tl	Tl	Tl	Tl	Tl	Tl
	Al	Al	Al	Al	Al	Al	Al	Al	Al
	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb
	Sn	Sn	Sn	Sn	Sn	Sn	Sn	Sn	Sn
	In	In	In	In	In	In	In	In	In
	Fe	Fe	Fe	Fe	Fe	Fe	Fe	Fe	Fe
	Co	Co	Co	Co	Co	Co	Co	Cu	Cu
	Sb	Sb	Cu	Cu	Cu	Cu	Cu	Co	Co
	Cu	Cu	Sb	Sb	Sb	Sb	Sb	Sb	Sb
	Si	Si	Si	Ag	Si	Ag	Ag	Ag	Ag
	Bi	Ag	Ag	Si	Ag	Hg	Hg	Hg	Hg
	Ni	Ni	Hg	Bi	Bi	Si	Bi	Bi	Bi
	Ag	Bi	Bi	Hg	Hg	Bi	Si	Si	Si
	Hg	Hg	Ni	Ni	Ni	Ni	Ni	Ni	Ni
	Pd	Pd	Pd	Pd	Pd	Pd	Pd	Pd	Pd
	Au	Au	Te	Te	Au	Au	Te	Au	Au
	Te	Te	Au	Au	Te	Te	Au	Te	Te
	Pt	Pt	Pt	Pt	Pt	Pt	Pt	Pt	Pt
	Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir
	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh
	C	C	C	C	C	C	C	C	C.

VI.

DEGREES OF CONCENTRATION.   TEMPERATURE = 37°.78 C.
1879.)

31.10%	36.28%	41.47%	46.65%	51.84%	64.80%	77.76%	103.6%	129 6%	Satu-rated.
Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg
Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn
Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd
Tl	Tl	Tl	Tl	Tl	Tl	Tl	Tl	Tl	Tl
Al	Al	Al	Al	Al	Al	Al	Al	Al	Al
Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb
Sn	Sn	Sn	Sn	Sn	Sn	Sn	Sn	Sn	Sn
In	In	In	In	In	In	In	In	In	In
Fe	Fe	Fe	Fe	Cu	Cu	Cu	Cu	Cu	Cu
Cu	Cu	Cu	Cu	Ag	Ag	Ag	Ag	Ag	Ag
Co	Co	Ag	Ag	Fe	Fe	Fe	Sb	Fe	Sb
Sb	Ag	Sb	Sb	Sb	Sb	Sb	Fe	Hg	Fe
Ag	Sb	Co	Co	Hg	Hg	Hg	Hg	Sb	Hg
Hg	Hg	Hg	Hg	Co	Co	Co	Co	Co	Co
Bi	Bi	Bi	Bi	Bi	Bi	Bi	Bi	Bi	Bi
Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
Ni	Ni	Ni	Ni	Ni	Ni	Ni	Ni	Ni	Ni
Pd	Pd	Pd	Pd	Pd	Pd	Pd	Pd	Pd	Pd
Au	Au	Au	Au	Au	Au	Au	Au	Te	Te
Te	Te	Te	Te	Te	Te	Pt	Te	Au	Au
Pt	Pt	Pt	Pt	Pt	Pt	Te	Pt	Pt	Pt
Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir
Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh
C	C	C	C	C	C	C	C	C	C

SOLUTIONS OF CYANIDE OF POTASSIUM AT DIFFERENT
(G. GORE,

Quantity of CyK.	0.130%	0.324%	1.296%	2.592%	5.184%	10.37%	15.55%	20.75%
	Mg	Al	Mg	Mg	Al	Al	Al	Mg
	Zn	Mg	Zn	Zn	Mg	Zn	Zn	Al
	Al	Zn	Al	Al	Zn	Cu	Mg	Zn
	Cd	Cu	Cu	Cu	Cu	Mg	Cu	Cu
	Cu	Cd	Cd	Cd	Cd	Cd	Cd	Cd
	Sn	Sn	Au	Au	Pd	Au	Ag	Au
	Tl	Co	Ag	Pd	Ag	Pd	Au	Pd
	Pb	Ni	Sn	Ag	Au	Ag	Pd	Ag
	Co	Ag	Co	Co	Co	Ni	Ni	Ni
	In	In	Ni	Ni	Ni	Co	Hg	Sn
	Au	Au	Pd	Sn	Pb	Pb	Co	Pb
	Ag	Tl	Tl	Tl	Tl	Tl	Sn	Co
	Sb	Hg	Pb	Pb	Hg	Hg	Pb	Hg
	Ni	Pb	In	Hg	Sb	Sb	In	Tl
	Hg	Si	Sb	In	Sn	Sn	Tl	In
	Pd	Fe	Hg	Sb	In	In	Sb	Sb
	Fe	Pt	Bi	Bi	Bi	Bi	Bi	Te
	Bi	Pd	Te	Fe	Te	Te	Te	Bi
	Pt	Sb	Fe	Si	Si	Fe	Fe	Si
	Te	Bi	Si	Te	Ir	Ir	Si	Fe
	Si	Ir	Pt	Pt	Fe	Si	Ir	Ir
	Ir	Te	Ir	Ir	Pt	Pt	Pt	Pt
	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh
	C	C	C	C	C	C	C	C

VII.

DEGREES OF CONCENTRATION. TEMPERATURE = 12°.78 C. 1879.)

25.92%	31.10%	36.28%	41.47%	46.65%	51.84%	64.80%	Satu-rated.
Mg	Mg	Mg	Mg	Mg	Zn	Zn	Zn
Zn	Zn	Zn	Zn	Zn	Cu	Mg	Cu
Al	Cu	Cu	Cu	Cu	Mg	Cu	Mg
Cu	Al	Al	Al	Al	Cd	Cd	Cd
Cd	Cd	Cd	Cd	Cd	Al	Al	Al
Au	Au	Ag	Ag	Ag	Pd	Pd	Pd
Ni	Ag	Au	Au	Au	Ni	Ag	Au
Ag	Pd	Pd	Ni	Ni	Au	Au	Ag
Pd	Ni	Ni	Pd	Pd	Ag	Ni	Ni
Sn	Sn	Sn	Hg	Sn	Sn	Sn	Sn
Hg	Hg	Hg	Sn	Hg	Pb	Hg	Hg
Pb	Pb	Pb	Pb	Pb	Co	Pb	Co
Co	Co	Co	Co	Co	Hg	Co	Pb
Sb	Sb	Tl	Sb	Tl	Tl	Tl	In
Tl	Tl	Sb	Tl	Sb	Sb	In	Tl
In	In	In	In	In	In	Sb	Te
Te	Te	Te	Te	Te	Te	Te	Sb
Bi	Bi	Bi	Bi	Bi	Bi	Bi	Bi
Si	Si	Si	Fe	Fe	Fe	Fe	Fe
Pt	Fe	Fe	Si	Si	Si	Si	Si
Fe	Pt	Pt	Pt	Pt	Pt	Pt	Pt
Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir
Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh
C	C	C	C	C	C	C	C

Position of Aluminium in the Voltaic Series (Wheatstone, 1855).—Aluminium placed in a solution of potash is negative* to zinc and positive to the following metals : cadmium, tin, lead, iron, copper, and platinum. A solution of potash acts more energetically and with a greater disengagement of hydrogen on aluminium than on zinc. The most constant couple is aluminium–copper. Other metals associated with aluminium polarize rapidly.

Aluminium in a solution of hydrochloric acid is negative to zinc and to cadmium, and positive to the following metals : copper, tin, lead, iron, and platinum. The most constant couple is aluminium–copper.

In dilute nitric acid aluminium is negative to the following metals : zinc, cadmium, tin, lead, and iron. With zinc the current is very strong ; with other metals it is, on the contrary, very weak.

In dilute sulphuric acid aluminium is negative to zinc, cadmium, tin, and iron. When the surface is clean, aluminium in dilute phosphoric acid or in ordinary water is positive to iron, copper, silver, and platinum. When associated with lead, aluminium gives no current. Copper and platinum are negative to aluminium, whether in dilute nitric or sulphuric acid. According to Wheatstone aluminium does not always hold the same position in the voltaic series. These variations are due, according to Heeren (1855), to a sort of passivity of the metals produced either by a thin layer of oxide or by a deposit of hydrogen.   In fact, Buff (1857) has shown that aluminium becomes passive when placed in nitric acid whatever may be the state of concentration of the latter.

THE AMALGAMATION OF ZINC.

The first account of amalgamated zinc is in Sir Humphry Davy's Bakerian Lecture for 1826, where he states that " zinc in amalgamation with mercury is positive with respect to pure zinc," without reference to its use in the voltaic cell. Kemp

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* Terms reversed in this paragraph to accord with general definitions of this book.

of Edinburgh (New. Edin. Phil. Jour. 1828) was the first to employ amalgamated zinc and copper in this apparatus, where, he says, "the amalgam of zinc and mercury becomes the positive plate, while the copper is rendered negative." The invention is also claimed by Sturgeon (1840), who says : " I believe that the employment of amalgamated rolled zinc originated with my own experiments, and I formed compound batteries of cylinders of zinc and copper which worked exceedingly well with diluted sulphuric acid."

The singular property possessed by amalgamated zinc of not being attacked in sulphuric acid diluted with water is due to the adhesion of hydrogen on the plate in the acid solution. De la Rive (1848) observed that amalgamated zinc in water acidulated with $\frac{1}{30}$ of its volume of sulphuric acid soon ceases to be attacked, ordinary atmospheric pressures prevailing ; that if a vacuum is made above the liquid, hydrogen-bubbles in abundance are disengaged anew ; and that if the air be readmitted to the cell, the gas-bubbles still adhering to the metal soon become flattened and the chemical action stops.

If a plate of ordinary zinc and a plate of amalgamated zinc be placed in acidulated water and connected by a copper wire, the amalgamated plate acts like the zinc and the other like the copper in the ordinary voltaic cell. Thus the plate of amalgamated zinc acts like a metal more strongly attacked by acidulated water than ordinary zinc.

Robb (1883) has shown, however, that if care be taken to use pure zinc obtained electrolytically (like solutions of sulphate which have remained free from carbonate of zinc, and which have thus been deprived of all free acid), the couple Zinc–zinc^{Hg} exhibits no sensible electromotive force.

The element cadmium–cadmium^{Hg}, solution of cadmium sulphate, shows, on the contrary, a notable electromotive force. Pure cadmium is dissolved and is carried, by the effect of the current, upon the amalgamated cadmium. A curious fact noted by Regnault is, that while the amalgamation of zinc is attended with an absorption of heat, a disengagement of heat follows the amalgamation of cadmium.

Influence of Amalgamation on the Electromotive Force of Metals.—Wheatstone and Regnault have found that the proportion of metal contained in an amalgam does not affect the electromotive force of the couples of which the amalgam forms a part. Gaugain (1856), however, has observed that this is not the case in all combinations. In the single-liquid cell containing zinc–mercury, sulphate of zinc, the zinc is positive* to the mercury, and the electromotive force of the couple exceeds 1 volt when the mercury is pure. But if increasing quantities of zinc be gradually introduced into the mercury, the electromotive force of the couple diminishes rapidly, and for a very small proportion of zinc becomes *nil.* If this proportion be augmented, the electromotive force changes sign, the amalgam becomes positive to the zinc, and the absolute value of the electromotive force increases with the proportion of zinc so long as this proportion does not exceed a certain limit, beyond which newly introduced quantities of zinc do not further alter the electromotive force, which is then about 0.05 volt.

In the class of couples represented by cadmium, cadmium amalgam, sulphate of cadmium, the direction of the current is independent of the proportions of the amalgam. The cadmium is always positive, but the electromotive force may vary within quite extended limits, from 0.025 volt (solid amalgam) to 0.16 volt (pure mercury).

$$\overset{+}{\text{Zinc}}-\overset{-}{\text{mercury}}, \text{ sulphate of zinc} \ldots\ldots\ldots\ldots\ldots = 1.08 \text{ volt.}$$

$$\overset{-}{\text{Zinc}}-\overset{+}{\text{amalgam}} \text{ of liquid zinc, sulphate of zinc}\ldots = 0.05 \text{ "}$$

$$\overset{-}{\text{Zinc}}-\overset{+}{\text{amalgam}} \text{ of solid zinc, sulphate of zinc}\ldots\ldots = 0.04 \text{ "}$$

$$\overset{+}{\text{Cadmium}}-\text{amalgam of cadmium, sulphate of cad-}$$
mium.................................... = 0.025 "

Cadmium–mercury, sulphate of cadmium........ = 0.16 "

(Gaugain.)

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* Terms reversed in this paragraph to accord with general definitions of this book.

Methods of Amalgamation of Zinc. — According to Vergnes, this may be done in the following manner : Take five parts of lead and one of mercury. Melt the lead, and while it is liquid cover it with a layer of fat or resin. Allow it to cool partly. Add the mercury and agitate the mixture. When it is completely cooled, a pasty mass will result having the consistence of soft wax. This may be rubbed with a brush upon the zinc plates to be amalgamated.

Colletet proposes rubbing the zincs with sodium amalgam in slightly acidulated water. Tommasi obtains very good amalgamation by rubbing them with a brush impregnated with a paste formed of bisulphate of mercury, fine sand, and dilute sulphuric acid. Berjot immerses the zincs in a concentrated solution of mercuric nitrate added to its volume of hydrochloric acid.

Amalgamated Iron.—According to Boettger, this is obtained by heating iron in a porcelain vessel with a mixture of 12 parts mercury, 1 part zinc, 2 parts sulphate of iron, 12 parts water, and 1.5 parts hydrochloric acid. The amalgamation takes place with an absorption of heat. Lecyre proposes the following process : On the iron, previously well cleaned, there is poured a solution of chloride of copper in hydrochloric acid ; this produces a thin layer of copper on the iron. The latter is then placed in a solution of mercuric chloride to which hydrochloric acid is added.

M. Reynier has made a number of tests of zinc, variously prepared, immersed in different liquids, the results of which are given in the table on the next page. He adds the following observations : Zinc alloyed with mercury is in general better than amalgamated zinc, especially in experiments of long duration. On amalgamated zinc the first superficial layer is rich in mercury; but as the deeper layers are attacked the proportion of mercury diminishes. With the alloy the contrary is the case, the mass becoming richer in mercury as its weight decreases. The presence of free nitric acid (in mixtures of acidulated water and sodium nitrate) considerably augments the attack on the zincs.

The utility of amalgamating the zincs in cells of the

TESTS OF ZINCS VARIOUSLY PREPARED, IMMERSED IN DIFFERENT LIQUIDS. (E. REYNIER, 1884.)

Liquid.	Duration of Experiments. Hours.	Average in Milligrams per Hour and per Square Centimeter.		
		Ordinary Zinc.	Zinc amalgamated at the Surface.	Zinc amalgamated in the Mass.
Water...................... 900 c. cm.	1	990	....	....
Sulph. acid ordinary at 66°.. 100 c. cm.	72	....	18	2.2
Water .. .. 900 c. cm.	1	639	....	....
Sulph. acid, from sulphur, 66° 100 c. cm.	96	....	0.09	0.1
Water .... 900 c. cm.	1	78	....	....
Ordinary sulph. acid prepared with ore by the	3	307	....	....
D'Arsonval process .... 100 c. cm.	72	....	0.2	0.27
Water...................... 900 c. cm.	1	1265	....	....
Sulph. acid ord. at 66° ...... 100 c. cm.	24	....	4	2.7
Nitrate of sodium........... 50 g.	48	....	24	8.7
Water...................... 900 c. cm.	21	67	0.14	0.76
Sulph. acid ord. at 66° ...... 100 c. cm. {	93	....	0.71	0.62
	237	...	0.61	0.46
Sulphate of ammonium...... 50 g.	434	....	0.55	0.40
Water...................... 1000 g.	24	28	....	....
Bisulphate of potassium..... 100 g.	72	....	0.09	0.04
Water .... 1000 g.				
Bisulphate of potassium..... 100 g.	24	21.7	Inappreciable	Inappreciable
Sulphate of ammonium...... 50 g.	72	....		
Water .... 900 g.				
Sulph. acid at 66°........... 100 c. cm.	1	1566	1415	....
Sulphate of copper.......... 50 g.	130 m.	....	....	798
Water .... 1000 g.	24	39	15	19
Sulphate of copper.......... 150 g.	48	....	26	28
Water...................... 1250 g.	30 m.	2603	....	....
Bichromate of potassium.... 200 g.	130 m.	....	634	....
Sulph. acid ord. at 66° ...... 470 g.	3	....	....	445
Hydrochloric acid (commerc.) {	15 m.	6555	....	....
	24	....	61	11
Water............. .... 800 c. cm.	1	1519	....	....
Hydrochloric acid (commerc.) 200 c. cm.	72	....	0.87	0.3

Daniell type is frequently disputed ; but experiment shows that mercury reduces the loss by half in a 15 per cent sulphate of copper solution. In a chromic mixture, amalgamated zinc

soon loses its brilliancy and becomes blackish, while the alloy, on the other hand, becomes brighter as it is used.

CAUSES AFFECTING THE E. M. F. OF VOLTAIC CELLS.

Action of Pulverized Carbon packed around Carbon Electrodes.—Retort-carbon may develop, under certain con-ditions, an electromotive force which, while not the same for al! carbons, may vary but little for a given carbon the physi-cal state of which remains unaltered. If from a selection of such carbons two highly electro-positive pieces and two highly electro-negative pieces be respectively ground and mixed with water, and the compound packed around two carbon electrodes, it will be found that the carbon mixture in proximity to the electrode of like character at the beginning renders the latter negative if it be positive, or augments an already existing nega-tive polarity; but at the end of about fifteen minutes the con-trary effect supervenes and then the electrode becomes strongly positive if it is negative, or still more positive if it were origi-nally of that character. This effect, according to Du Moncel, is general whatever may be the polarity of the mixture, and continues momentarily even after the mixture no longer sur-rounds the electrode. The reason, therefore, is apparent why cells in which carbon electrodes are surrounded by pulverized carbon possess a superior electromotive force.

Leclanché finds that the best results are obtainable with coarsely ground carbon, on account of the finely pulverized material presenting a much higher resistance to the current. The effects of polarization when a fine powder is used appear rather on the surface of the electrode than upon the powder, while with the coarse substance the reverse is the case. These effects at the end of fifteen minutes are greater with fine powder than with coarse in the ratio of 0.300 to 0.082.

Influence of Dilution on the Electromotive Force of Batteries.—According to Helmholtz, when there is employed in the cell a salt which disengages heat on solution, the elec-tromotive force of the element should diminish with solutions more and more concentrated.

H. Jahn (1886) has shown that this theory is true at least for the element

Zinc, chloride of zinc—chloride of silver, silver.

(Chloride of zinc dissolving in water disengages 15.54 calories.)

Experiment gives the subjoined results for the following concentrations:

$$Cl_2Zn + 100 \ H_2O = 1.0306;$$
$$\text{``} \quad + \ 50 \quad \text{``} \quad = 1.0171;$$
$$\text{``} \quad + \ 25 \quad \text{``} \quad = 0.974.$$
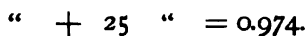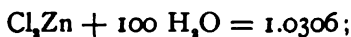
Influence of Porous Diaphragms.—J. Regnauld (1855) has shown that the most diverse materials (pipe-clay, unglazed porcelain of various thicknesses, wooden tubes, etc.) may be employed as the porous partition in cells of the Daniell type without modification of results. Viollet (1863) has proposed to incorporate in the paste of porous cells during process of manufacture a certain quantity of organic substances, which being eliminated during the firing of the ware renders the wall of the vessel spongy and of less resistance.

D'Arsonval (1881) has obtained excellent results by simply dipping the zinc in normal collodion. The collodion in drying forms a membrane without solution of continuity which resists acids and which can be rendered thicker by successive dippings. The same authority has made porous cups of asbestos paper, which he finds offer no resistance to the current, but which unfortunately disaggregates immediately in acids. This difficulty is somewhat lessened by giving the paper more body by dipping it in collodion.

Influence of Heat on the Electromotive Force of Batteries. (See also Heat Cells *ante*.)—This subject was investigated by Faraday (1840), Wild (1858), and Lindig (1868). Bleckrode (1871) placed two electrodes of the same metal in separate vessels, each containing a salt of the metal and connected by a siphon. One vessel was kept at substantially constant temperature, while the other was gradually heated.

In some instances the electromotive force was found to be proportional to the differences of temperature ; this appearing in the following couples :

Cold.	Hot.
Copper, sulphate of copper	—Copper, sulphate of copper.
Copper, nitrate of copper	—Copper, nitrate of copper.
Zinc^{Hg}, sulphate of zinc	—Zinc^{Hg}, sulphate of zinc.
Zinc^{Hg}, chloride of zinc	—Zinc^{Hg}, chloride of zinc.

Such a result, however, is rare.

In general the current goes through the siphon from the cold to the hot vessel, except with the couples :

Cold.	Hot.
Silver, nitrate of silver	— Silver, nitrate of silver.
Silver, acetate of silver	— Silver, acetate of silver.

In which the contrary direction is taken.

In other instances the current changes sign. Thus when amalgamated zinc is placed in a solution of double cyanide of zinc and potassium the current is at first positive, or from the cold to the hot vessel. It then changes sign when the difference of temperature exceeds 30° C. The same effect occurs at 53° C.; with silver in the double cyanide of silver and potassium.

Lead in nitrate of lead behaves still more singularly. The couple is at first negative, the current proceeding from the hot to the cold vessel. It changes sign when the difference of temperature exceeds 21° C., and then changes again and becomes once more negative when this difference reaches 51° C.

A. Voller (1873) has determined that the electromotive force increases about 5 per cent between 0° and 100° C. at the contact of platinum and nitric acid and at that of zinc and sulphuric acid, and 17 per cent between 21° and 78° C. at the contact of copper and chloride of sodium. On the contrary, the combinations (zinc–sulphate of zinc) and (zinc–chloride of sodium) show a diminution of 8 per cent between 28° and 90° C. ; the combination (copper–sulphate of copper) 0.43 per

cent between 22° and 91° C.; and the combination (copper-sulphate of zinc) 0.83 per cent between 25° and 80° C.

B. Lenz (1869) has observed that the electromotive proper-ties of electrolytic iron change under the action of heat. Heated iron behaves much like copper. In fact, a couple of iron (heated) and zinc placed in potash produces the same deviation ($+$ 114°) of the galvanometer as a couple of copper and zinc; while a couple of zinc and iron (not heated) pro-duced a smaller deviation ($+$91°). A couple formed of iron heated and iron not heated produced under the same condi-tions a deviation of $-$ 6°.

Influence of the Temperature and the Condition of the Metals on the Electromotive Force of Batteries.—If, in the Daniell element (zinc, sulphate of zinc–sulphate of cop-per, copper), says F. Raoult, there be used rolled copper or crystalline electrolytic copper rough or burnished, electrolytic zinc crystalline or powdered, or finally amalgamated zinc, the E. M. F. is the same in all cases within $\frac{1}{800}$, provided that the same be observed only when the metals are well moistened. Raoult (1869) has also examined whether the E. M. F. of bis-muth, tin, or lead is the same whether the condition of the metal be solid or liquid, and finds that there is no perceptible variation at the moment when the metal changes from one state to the other.

It will be observed from Favre's table, page 356, that the couple which yields the most confined heat is that with oxygen-ated water and hydrochloric acid, which comes from a combus-tion of hydrogen which is not utilized as in the other couples; that is to say, this heat is not transformed into electric energy. Hence, as M. Favre points out, the following important conse-quence, namely: the heat evolved during the combustion of the hydrogen reduced in electrolysis is transmissible or non-trans-missible to the circuit according to the nature of the compound which furnishes the oxygen necessary to this combustion.

Researches of D. Tommasi (1882).—1. It will be noted from the table on page 356 that a zinc-platinum, dilute sulphuric acid element would disengage, according to Favre, 39 calories:

RELATION BETWEEN THE CHEMICAL ENERGY AND THE E. M. F.
OF CERTAIN VOLTAIC COUPLES. (J. THOMSEN, 1880.)

Voltaic Couple.	Chemical Reaction.	Heat disengaged.	Energy of the Combination.	
			Absolute.	Daniell = 1.
		calories.	calories.	
Zinc.............. Sulphuric acid*.... Sulphate of copper.. Copper...........	+ (Zn, O, SO$_2$Aq) − (Cu, O, SO$_2$Aq)	+ 106.090 − 55.960	50.13	1
Zinc............. Sulphuric acid*.... Sulphate of cadm... Cadmium.........	+ (Zn, O, SO$_2$Aq) − (Cd, O, SO$_2$Aq)	+ 106.090 − 89.500	16.59	0.33
Zinc.............. Hydrochloric acid*. Chloride of silver .. Silver............	+ (Zn, Cl$_2$Aq) − (Ag$_2$, Cl$_2$)	+ 112.810 − 58.760	54.08	1.08
Zinc.............. Sulphuric acid *.... Nitric acid......... Carbon...........	+ (Zn, O, SO$_2$Aq) − (N$_2$O$_4$, O, H$_2$O)	+ 106.090 − 10.010	96.08	1.92
Zinc.............. Sulphuric acid*.... Nitric acid*....... Carbon...........	+ (Zn, O, SO$_2$Aq) − ½(N$_2$O$_2$, O$_3$, 7H$_2$O)	+ 106.090 − 23.280	82.81	1.65
Zinc.............. Sulphuric acid*.... Chromic acid...... Carbon...........	+ (Zn, O, SO$_2$Aq) − ½(Cr$_2$O$_3$, O$_3$Aq)	+ 106 090 − 6.300	99.780	1.99
Copper........... Sulphuric acid*.... Nitric acid......... Carbon...........	+ (Cu, O, SO$_2$Aq) − (N$_2$O$_4$, O, H$_2$O)	+ 55.960 − 10.010	45.95	0.92
Iron.............. Hydrochloric acid*. Ferric chloride..... Carbon...........	+ (Fe$_2$, Cl$_2$, Aq) − (Fe$_2$Cl$_4$, AqCl$_2$)	+ 99.950 − 55.520	44.43	0.89
Zinc.............. Sulphuric acid*.... Platinum..........	+ (Zn, O, SO$_2$Aq) − H$_2$O	+ 106.090 − 68.360	37.73	0.75

* Diluted.

RELATION BETWEEN THE CHEMICAL ENERGY AND THE ELECTRIC ENERGY OF VOLTAIC COUPLES.

(H. JAHN, 1886.)

Voltaic Couples.	Electromotive Force at o° C.	Electric Energy in Calories.	Chemical Energy in Calories.	Coefficient of Temperature.	Free Heat Disengaged. Observed.	Free Heat Disengaged. Calculated.
	volts.					
Copper, sulphate of copper + 100H$_2$O / Zinc, sulphate of zinc + 100H$_2$O	1.0962	50.526	50.110	+0.000034	−0.416	−0.428
Copper, acetate of copper saturated / Lead, acetate of lead + 100H$_2$O ...	0.47643	21.96	16.523	+0.000385	−5.437	−4.844
Silver, chloride of silver / Zinc, chloride of zinc + 50H$_2$O	1.0306	47.506	52.17	−0.000429	+4.66	+5.148
Silver, chloride of silver / Zinc, chloride of zinc + 100H$_2$O	1.0171	46.896	49.082	−0.000021	+2.186	+2.644
Silver, chloride of silver / Zinc, chloride of zinc + 25H$_2$O	0.9740	44.903	47.147	−0.000202	+2.239	+2.54
Silver, bromide of silver / Zinc, bromide of zinc + 25H$_2$O	0.84095	38.772	39.936	−0.000105	+1.164	+1.334

TABLE OF CALORIES PRODUCED WITHIN CELLS, TRANSMISSIBLE TO THE CIRCUIT. (FAVRE.)

Cells.	Q	Q^1	Q^2
	calories	calories	calories
Couple with hypochlorous acid.....................	101.6	24.0	125.6
" Grove, with fuming nitric acid	99.6	5.6	105.4
" " " ordinary " "	92.8	−9.8	82.8
" with permanganic and sulphuric acids, mixed...................................	78.4	42.8	121.2
" with mercuric sulphate....................	58.6	16.4	75.0
" Daniell..................................	47.8	2.0	50.0
" with chromic and sulphuric acids, mixed ..	60.4	56.8	117.2
" " oxygenated water and hydrochloric acid	41.6	89.4	131.0
" Smee with hydrochloric acid..............	33.4	1.2	....
" " " hydrobromic "	29.8	5.8	....
" " " hydroiodic "	29.0	6.6	....
" " " sulphuric "	29.8	9.0	....
" with sulphate of copper and hydrogen and platinum (alloyed), with acidulated water and hydrogen acting as electro-positive metal...	8.0	11.6	....

Q = quantity of heat transmissible to the circuit, representing the energy of the cell.

Q^1 = quantity of heat confined in the cell.

Q^2 = quantity of heat corresponding to the reduction of the depolarizing liquid.

but that of these only 29.8 calories would be transmissible to the circuit, and hence would represent the energy of the cell. Hence it would follow that two of these cells could not decompose water. Thus

$$29.8 \text{ cal.} + 29.8 \text{ cal.} < 69 \text{ cal. (1.49 volts).}$$

Now, M. Tommasi observes that this decomposition would take place, as is well known, if all the calories disengaged by both couples could be transmitted to the circuit. Thus:

$$39 \text{ cal.} + 39 \text{ cal.} > 69 \text{ cal.} \quad \text{(Favre.)}$$
$$38 \text{ cal.} + 38 \text{ cal.} + 1.4 \text{ cal.} > 69.$$

(This last is calculated according to the latest thermic data. The E. M. F. of a couple of amalgamated zinc and dilute sulphuric acid would be greater than that of the zinc couple by about 0.7 cal.)

If the water of the voltameter is acidulated with hydrochloric acid, the decomposition of the water takes place more rapidly, as might easily be anticipated from the fact that the electrolysis of dilute hydrochloric acid absorbs, for two molecules, 66 calories, in place of 69. But even in this case there would be, according to Favre, no electrolysis, for

$$29.8 \text{ cal.} + 29.8 \text{ cal.} < 66 \text{ cal.}$$

2. According to Favre, two zinc-platinum and hydrochloric acid couples cannot decompose water if it be acidulated with H_2SO_4, but can do so if it be acidulated with HCl. In the first case we have

$$33.4 \text{ cal.} + 33.4 \text{ cal.} < 69 \text{ cal.,}^*$$

and in the second,

$$33.4 \text{ cal.} + 3.4 \text{ cal.} > 66 \text{ cal.}$$

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* According to Favre, this couple would in fact disengage 34.8 cal., but only 33.4 cal. would be transmissible to the circuit.

3. According to Favre, the couple with chromic acid and sulphuric acid mixed* would disengage 117.3 cal. (2.5 volts), but 62.5 cal. (1.35 volts) only would be transmissible to the circuit. Hence it would follow that a single chromic acid couple could not decompose water acidulated by sulphuric acid.

In fact, if the negative electrode of this element is of platinum, water is not decomposed; but if the electrode is of carbon or platinum sponge, water is electrolyzed. The chemical reaction in the interior of this couple being always the same, M. Tommasi has endeavored to determine approximately by means of electrolysis the number of calories transmissible to the circuit by the chromic acid couple, according as its negative electrode is platinum, carbon, or platinum sponge, and has obtained the following results:

1. The chromic acid couple as employed by Favre—that is, having its negative electrode of platinum—produces an external chemical work of only about 65 cal. (1.4 volts).

2. By substituting for platinum in the same couple carbon or platinum sponge, about 80 calories (1.8 volts) become transmissible to the circuit.

Researches of F. Raoult (1863).—Favre has shown that in the Daniell element the heat produced by the current is nearly equal to that disengaged by chemical action. According to Raoult, this is true only of the Daniell element. In others, he says, the heat produced by the current in the entire circuit and the heat produced by the chemical reaction are often notably different. The following are some of the results obtained:

	Heat.	
	Chemical.	Voltaic.
Zinc, sulphate of zinc—sulphate of copper, copper	23.56 cal.	23.6 cal.
Zinc, acetate of zinc—acetate of lead, lead	15.7 "	12.4 "
Copper, nitrate of copper—nitrate of silver, silver	16.4 "	7.8 "

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* This couple is composed of a glass outer vessel containing an amalgamated zinc placed in water acidulated with H_2SO_4 and a porous jar containing the following mixture: Chromic acid, 25 grams; water, 50 c. cm.; sulphuric acid, 10 c. cm.

Whence it follows, says M. Raoult, that, from the point of view of aptitude to produce electricity, the chemical actions in batteries play two parts: the one, composed of actions exerted between unlike molecules (combinations and decompositions), produces current; the other, composed of actions exerted between like molecules (disaggregation, diffusion, and inverse effects), does not.

Effects of Different Positive Metals, etc., upon the Changes of Potential of Voltaic Couples. (Gore, 1887.)

In this research numerous measurements were made, and these are given in a series of tables of the effects upon the minimumpoint of change of potential of a voltaic couple in distilled water (Roy. Soc. Proc., June 14, 1888), and upon the changes of electromotive force attending variation of strength of its exciting liquid (*ibid.*) obtained by varying the kind of positive and of negative metal of the couple, and by employing different galvanometers. The measurements were made by the method of balance through a galvanometer, with the aid of a suitable thermo electric pile (Birmingham Philos. Soc. Proc., vol. 4, p. 130; the *Electrician*, vol. ii. p. 414). The kinds of galvanometer employed were an ordinary astatic one of 100 ohms resistance and a Thomson's reflecting one of 3040 ohms resistance.

The following were the proportions of hydrochloric acid (HCl) required to change the potential of different voltaic couples in water:

TABLE 1. HYDROCHLORIC ACID

Astatic galvanometer.

Zn + Pt..............	Between 1 in 9,300,000	and	9,388,185
Cd + Pt..............	" 1 " 574,000	"	637,000
Mg + Pt..............	" 1 " 516,666	"	574,000
Al + Pt	" 1 " 12,109	"	15,000

Reflecting galvanometer.

Zn + Pt............	Between	1 in	15,500,000	and	23,250,000
Cd + Pt............	"	1 "	1,162,500	"	1,550,000
Mg + Pt	"	1 "	775,000	"	930,000
Al + Pt...........	"	1 "	42,568	"	46,500

With iodine and the astatic galvanometer the following proportions were required :

TABLE 2. IODINE.

Zn + Pt.............	Between	1 in	3,100,000	and	3,521,970
Mg + Pt.............	"	1 "	577,711	"	643,153
Cd + Pt.............	"	1 "	200,431	"	224,637

With bromine and the astatic galvanometer :

TABLE 3. BROMINE.

Mg + Pt.........	Between	1 in	310,000,000	and	344,444,444
Zn + Pt.........	"	1 "	77,500,000	"	84,545,000
Cd + Pt.........	"	1 "	3,470,112	"	3,875,000

The magnitudes of the minimum proportions of bromine required to change the potentials of the three couples in water varied directly as the atomic weights of the three positive metals.

With chlorine the following were the minimum proportions required :

TABLE 4. CHLORINE.

With the reflecting galvanometer.

Mg + Pt.....	Between	1 in	27,062,000,000	and	32,291,000,000

With the astatic galvanometer.

Mg + Pt.....	Between	1 in	17,000,000,000	and	17,612,000,000
Zn + Pt......	"	1 "	1,264,000,000	"	1,300,000,000
Zn + Au.....	"	1 "	518,587,360	"	550,513,022
Cd + Pt......	"	1 "	8,733,585	"	9,270,833
Zn + Cd....	"	1 "	55,436	"	76,467

In the case of chlorine, as well as that of bromine, the magnitudes of the minimum proportions of substance required to change the potential of magnesium-platinum, zinc-platinum, and cadmium-platinum varied directly as the atomic weights of the positive metals.

The examples contained in the paper show that the proportion of the same exciting liquid necessary to disturb the potential of a voltaic couple in water varied with each different positive or negative metal, and that the more positive or more easily corroded the positive metal, or the more negative and less easily corroded the negative one, the smaller usually was the minimum proportion of dissolved substance necessary to change the potential.

By plotting the results in all cases, it was found that the order of change of potential, caused by uniform change of strength of liquid, varied with each positive metal.

The results also show that the degree of sensitiveness of the arrangement for detecting the minimum point of change of potential depends largely upon the kind of galvanometer employed.

As a more sensitive galvanometer enables us to detect a change of potential caused by a much smaller proportion of material, and as the proportion of substance capable of detection is smaller, the greater the free chemical energy of each of the uniting bodies (Roy. Soc. Proc., June 14, 1888), it is probable that the electromotive force really begins to change with the very smallest addition of the substance, and might be detected if our means of detection were sufficiently sensitive or the free chemical energy of the uniting bodies were sufficiently strong.

Voltaic Combinations in which Oxidizable Metals are Replaced by Alterable Solutions.

It appeared to Dr. C. R. Alder Wright and Mr. C. Thompson probable that just as a liquid capable of parting with oxygen, chlorine, etc., can be used in conjunction with an

electrode of unchangeable material at one side of a voltaic cell (as in Grove's nitric acid cell and analogous combinations), or may be replaced by a solid conducting electrode itself capable of losing oxygen (e.g., a plate of strongly compressed lead peroxide), so, conversely, might a conducting plate of oxidizable material (e.g., zinc) at the other side be replaced by an unchangeable electrode in conjunction with a liquid capable of taking up oxygen, chlorine, etc., without producing any fundamental change in the character of the actions taking place in the cell while generating a current. The electrode immersed in this oxidizable substance, like the zinc of an ordinary cell, would acquire a lower potential, and the opposed plate the higher potential; i.e., "the wire connected with the latter would be the 'positive pole' in reference to the external circuit." On trial it has been found that such is the case, and that in consequence a large variety of novel forms of cell results. For example, sodium sulphate or potassium ferrocyanide solution opposed to chromic-sulphuric acid solution: preferably with an intermediate layer of some neutral salt solution, such as sodium sulphate, to prevent the direct action of the two fluids on one another. During the passage of a current, sodium sulphate or potassium ferrocyanide is formed in quantity proportionate to the electricity passing, i.e., to the amount of silver thrown down in a silver voltameter included in the circuit, whilst chromium sulphate is produced at the other side. Various analogous cells are described, in particular one where lead oxide dissolved in caustic soda is opposed to alkaline hypobromite (in this case lead dioxide is produced and separates out in solid form), and one where chromium sesquioxide dissolved in caustic soda is opposed to chromium trioxide dissolved in sulphuric acid. Here sodium chromate and chromium sulphate are formed an E. M. F. about equal to that of Daniell's cell being set up.

CHAPTER XVIII.

GENERAL PRACTICAL DATA. (*Continued.*)

VARIOUS ELECTROMOTIVE FORCES.

E. M. F.'s of Carbon and Metals in their Contact with Distilled Water. (Becquerel, 1870.)

$$\text{Pure Water} \quad \begin{cases} \text{Carbon} \\ \text{Carbon} \end{cases}$$

NO current. The carbon was made in cylinders and by the decomposition of sugar-candy. The hydrogen products contained in the carbon were removed by chlorine, the chlorine by hydrogen, and the last by boiling water.

$$\text{Pure Water} \quad \begin{cases} \text{Carbon (heated)} - \\ \text{Carbon} + \end{cases}$$

One of the carbons was removed and heated in a platinum tube from 100° to redness, then replaced in the water. It had become negative*—a condition which results from the property which carbon possesses when it has absorbed air, of slowly producing carbonic acid. The carbon itself is thus rendered negative and the water positive.

If two platinum electrodes taken from the same piece of metal are substituted for carbon in pure water, no current results. If one be withdrawn and exposed to a current of hydrogen, it becomes negative; if exposed to a current of oxygen, positive. If exposed successively to the action of both gases, it becomes negative. If a platinum wire be subjected to a temperature of '100° C. in a heated tube for several minutes, it becomes negative, and after prolonging the heating it becomes positive on

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* Signs as given by Author.

contact with water. Removed from the water and heated for a few moments to a little less than red heat, it again becomes negative, then positive when heated to bright red, cooled and plunged in distilled water. When heated for a short time in boiling distilled water it quite frequently loses its polarity.

According to Becquerel, these results are explained only on the following hypotheses:

1. The decomposition of the vapor of atmospheric water or of water under the influence of the metal at a more or less elevated temperature.

2. A difference in the absorbing power of hydrogen and oxygen during the heating action. When this action is prolonged out of contact with water, hydrogen is disengaged, the air is absorbed during cooling, and the metal then becomes positive on contact with water by reason of the action of oxygen. Gold, palladium, and iridium act very nearly like platinum.

Electrodes of spongy platinum were placed in dilute nitric acid. Both were first heated to bright redness and then one of them, after cooling, was plunged in the acid, followed a few seconds later by the other. The electrode last immersed was negative. With concentrated nitric acid it is scarcely possible to determine the E. M. F., because of the rapid oscillations of the voltmeter needle.

With hydrochloric acid, concentrated or dilute, the effect is constantly inverse, that is, the electrode last immersed is always positive with concentrated acid, and the E. M. F. equals about 0.0131 volt. The effects are the same with pure sulphuric acid diluted with an equal volume of water, The E. M. F. equals 0.105 volt. With ammonia the last electrode immersed is also positive and the E. M. F. equals 0.246 volt.

E. M. F. of Platinum in Contact with Acidulated or Alkalinized Water (Gaugain, 1869).—Two plates of platinum were immersed in acidulated water for some time. One being withdrawn, washed in distilled water, and returned, was found to be negative.* E. M. F. = 0.0136 volt. Water alkalinized with KHO was then substituted. The washed and returned plate

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* Signs as given by author.

was then found to be positive. Identical results were obtained
with plates of platinized platinum.

It is possible to recognize by this means whether a liquid
is neutral, acid, or alkaline even when its reaction is so weak
as not to affect the ordinary test papers. In this case, how-
ever, non-platinized electrodes must be used.

The plates can be brought back to their original state by
simply wiping from their surfaces the deposit left after immer-
sion.

According to D. Macaluso (1873), the E. M. F. of platinum
placed in a solution of hydrochloric acid to which traces of
free chlorine are added increases rapidly to a maximum which
may reach 0.6 to 0.7 volt.

E. M. F. of Platinized Platinum.—It appears from the
experiments of Gaugain that platinized platinum is more
electro-negative than ordinary platinum without deposit. A
plate of platinum and a plate of platinized platinum form a
couple the E. M. F. of which may reach, at the instant of
immersion of the plates, 0.25 volt.

E. M. F.'S PRODUCED BY THE ACTION OF WATER ON SUL-
  PHURIC ACID AT DIFFERENT DEGREES OF HYDRATION.
  (BECQUEREL.)

Platinum Electrodes.

Sulphuric Acid. + *	Distilled Water. −	E. M. F.'s.
SO_4H_2, H_2O ....Aq..........		0.293 volt.
$SO_4H_2, 2H_2O$.......... "		0.191 "
$SO_4H_2, 3H_2O$.......... "		0.171 "
$SO_4H_2, 4H_2O$.......... "		0.141 "
$SO_4H_2, 5H_2O$.......... "		0.119 "
$SO_4H_2, 6H_2O$.......... "		0.102 "
$SO_4H_2, 7H_2O$.......... "		0.095 "
$SO_4H_2, 8H_2O$.......... "		0.089 "
$SO_4H_2, 9H_2O$.......... "		0.085 "
$SO_4H_2, 10H_2O$.......... "		0.082 "

* Signs as given by author.

Gold Electrodes.

Solution of Potash.	Distilled Water.	E. M. F.'s.
−	+	
$K_2O, 4H_2O$ .... Aq		0.310 volt.
$K_2O, 5H_2O$ .. .. "		C.217 "
$K_2O, 6H_2O$ .... "		0.201 "
$K_2O, 7H_2O$ .... "		0.181 "
$K_2O, 8H_2O$ .... "		0.165 "
$K_2O, 9H_2O$ .... "		0.154 "
$K_2O, 10H_2O$ .... "		0.143 "
$K_2O, 14H_2O$ .... "		0.133 "
$K_2O, 15H_2O$ .... "		0.132 "
$K_2O, 20H_2O$ .... "		0.125 "
$K_2O, 40H_2O$ .... "		0.122 "

E. M. F.'s PRODUCED BY THE ACTION OF WATER ON NITRIC
ACID AT DIFFERENT DEGREES OF HYDRATION.

Nitric Acid.	Distilled Water.	E. M. F.'s.
+	−	
N_2O_5, H_2O .... Aq		0.424 volt.
$N_2O_5, 2H_2O$ .... "		0.349 "
$N_2O_5, 3H_2O$ .... "		0.287 "
$N_2O_5, 4H_2O$ .... "		0.234 "
$N_2O_5, 5H_2O$ .... "		0.214 "
$N_2O_5, 6H_2O$ .... "		0.198 "
$N_2O_5, 7H_2O$ .... "		0.188 "
$N_2O_5, 8H_2O$ .... "		0.181 "

E. M. F.'s PRODUCED BY THE ACTION OF HYDRATED ACIDS
ON HYDRATED ALKALIES. (BECQUEREL.)

Gold Electrodes.

Nitric Acid.	Potash Solution.	E. M. F.'s.*
+	−	
$N_2O_5, 4H_2O$ ...... $K_2O, 4H_2O$		1.320 volts.
$N_2O_5, 6H_2O$ ...... $K_2O, 6H_2O$		1.104 "
$N_2O_5, 8H_2O$ ...... $K_2O, 8H_2O$		1.164 "

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* It should be observed that the E. M. F. produced by the action of sulphuric acid and nitric acid on potash is not in direct ratio to the heat developed by the action of these acids on potash. In fact, $2KHO + 2NO_3.H + Aq = 27.4$ cal. and $2KHO + SO_4H_2 + Aq = 31.7$ cal.

Sulphuric Acid.	Potash Solution.	E. M. F.'s.
$SO_3, 4H_2O$	$K_2O, 4H_2O$	0.768 volt.
$SO_3, 5H_2O$	$K_2O, 5H_2O$.........	0.686 "
$SO_3, 6H_2O$	$K_2O, 6H_2O$........	0.613 "
$SO_3, 7H_2O$	$K_2O, 7H_2O$........	0.590 "
$SO_3, 8H_2O$	$K_2O, 8H_2O$........	0.537 "
$SO_3, 9H_2O$.........	$K_2O, 9H_2O$........	0.501 "
$SO_3, 10H_2O$.......	$K_2O, 10H_2O$......	0.471 "
$SO_3, 20H_2O$.......	$K_2O, 20H_2O$......	0.435 "

E. M. F.'s produced by the Action of Saline Solutions on one another, as well as those resulting from the Action of Water on such Solutions.

[The apparatus employed in these researches consisted in a slit tube, the opening in which was about $\frac{1}{1000}$ of a milimetre in width and which contained one of the solutions ; and a test-tube containing the other solution. In each solution was placed a plate of gold or silver well cleaned and completely depolarized.]

I.

	Electric Condition of the Couples.*		E. M. F.'s.
1st couple	$\begin{cases} \text{Ammonium sulphate} \\ \text{Distilled water} \end{cases}$	$\begin{cases} - \\ + \end{cases}$	$\Big\}$ 0.066 volt.
2d couple	$\begin{cases} \text{Sodium carbonate} \\ \text{Distilled water} \end{cases}$	$\begin{cases} - \\ + \end{cases}$	$\Big\}$ 0.128 "
3d couple	$\begin{cases} \text{Ammonium sulphate} \\ \text{Sodium carbonate} \end{cases}$	$\begin{cases} + \\ - \end{cases}$	$\Big\}$ 0.065 "

The first two couples produce two currents in opposite directions. For the difference in the E. M. F.'s we have $0.128 - 0.066 = 0.062$,—very nearly 0.065.

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* Signs as given by Becquerel.

II.

	Electric Condition of the Couples.	E. M. F.'s.
1st couple {	Sodium carbonate − } Copper nitrate + }	0.211 volt.
2d couple {	Sodium carbonate − } Distilled water + }	0.128 "

The sum of the E. M. F.'s of couples 2 and 3 being due to both currents in the same direction, their resultant equals their sum, and we have

$$0.128 \text{ volt} + 0.075 \text{ volt} = 0.203 \text{ volt},$$

instead of 0.211, which gives the direct reaction of the two solutions, one with the other.

III.

	Electric Condition of the Couples.	E. M. F.'s.
1st couple {	Ammonium sulphate + } Barium chloride − }	0.027 volt.
2d couple {	Ammonium sulphate − } Distilled water + }	0.066 "
3d couple {	Barium chloride − } Distilled water + }	0.036 "

Currents obtained with couples 2 and 3 being directed oppositely, the resultant is their difference, which is equal to

$$0.066 \text{ volt} - 0.0363 \text{ volt} = 0.0297 \text{ volt}.$$

Becquerel (see page 370) deduced from these experiments that when a neutral solution reacts equally on another, the resultant E. M. F. of this reaction is equal to the sum or to the difference of the E. M. F.'s in the reaction of each of the solutions on the water of the other solution.

If a plate of platinum is put in nitric acid and another in a solution of caustic potash which is in contact with the acid by means of a porous diaphragm, a marked current of electricity is produced as soon as communication is established, the alkali assuming negative and the acid positive electricity. The same arrangement, however, substituting sulphuric or hydrochloric acid produces but a very weak current. (Becquerel, 1838.)

The platinum in this experiment may be replaced by iron, copper, or zinc. Thus, if two plates of the same metal be placed respectively in sulphuric acid and a potash solution, or in hydrochloric acid and a potash solution, a very pronounced and constant current is observable, but one much more intense with zinc than with the other two metals. The energy augments when the sulphuric acid is diluted one half with water. In these experiments, the zinc plate in the acid, although much more chemically attacked than that in the alkali, always takes positive electricity, although it represents the copper in an ordinary voltaic combination. Similar phenomena appear with nitric acid, in which inactive iron, passive iron, zinc, and copper always take positive electricity in relation to the same metals in potash or in sulphuric and hydrochloric acids. (Grove, 1839.)

Electric Condition of Liquids in Contact. — Nitric acid is positive with hydrochloric acid, acetic acid, nitrous acid, alkaline solutions, nitrate solutions, sulphate solutions, neutral chloride solutions. Nitric acid is negative with sulphuric acid, phosphoric acid. Phosphoric acid is positive with hydrochloric acid, sulphuric acid, alkaline, saline solutions.

On the E. M. F.'s produced at the Contact of Liquids separated by Capillary Diaphragms. — The acid and the base are placed in contact by means of a diaphragm consisting either in a slit or cracked tube, or a tube closed by parchment-paper, or a porous cup. Under these conditions, it has been found that, with all the dilute acids (1 equivalent of acid or of base in 2 litres of water) experimented upon, the E. M. F. increases at first quite rapidly, then slowly, and finally, after a time more

E. M. F.'S DEVELOPED BY THE MUTUAL ACTION OF SOLUTIONS. (E. BECQUEREL.)

| Liquids of the Couple. | | Electrode placed Externally. | Electrode placed in the Porous Cup. | E. M. F.'s in volts. |
Outer Vessel.	Porous Cup.			
Water acidulated with $\frac{1}{16}$ sulphuric acid	Saturated solution of copper sulphate......	Platinum +	Platinum —	0.127
"　"　"　"	Oxygenated water (at 12 vols.)........	Platinum —	Platinum +	0.128
"　"　"　"	Saturated solution of chloride of platinum..	"	"	0.340
"　"　"　"	Nitric acid (36° B.)........	"	"	0.340
"　"　"　"	Sol. of chromic acid (1 p. water, 1 p. acid.).	"	"	0.472
"　"　"　"	Water saturated with chlorine at 14°	"	"	0.632
Solution of ferrous sulphate	"　"　"　"　"	"	"	0.799
Hydrochloric acid pure and concentr....	Nitric acid pure and concentrated.........	"	"	0.892
Solution of potash at 25%............	Nitric acid ordinary..................	"	"	0.943
Solution of persulph. of potassium at 5%	"　"	"	"	1.232
Solution of potash at 25%...........	"　"	Gold —	Gold +	0.756
"　"　"　"	"　"	Silver —	Silver +	0.756
"　"　"　"	"　"	Carbon —	Carbon +	1.020

* Signs as given by Becquerel.

or less long, attains a maximum, after which it weakens anew. Thus,

	Minimum.	Maximum.	
Nitric acid + potash	0.356 volt	0.636 volt,	after 2 days
Sulphuric acid + potash	0.336 "	0.448 "	" 1 day
Hydrochloric acid + potash..........	0.356 "	0.479 "	" 5 hours
Acetic acid + potash................	0.283 "	0.316 "	——
Phosphoric acid + potash...........	0.178 "	0.254 "	——

Disengagement of Electricity produced at the Contact of Solids and of Liquids in Motion (E. Becquerel, 1854).—In a cylindrical vessel of a diameter of 15 cm. are placed vertically the two plates or two metal wires to be tested (platinum, gold, copper, zinc, iron, etc.); the vessel is filled with the experimental solution. One of the plates is attached to the arm of a horizontal lever, which is set in uniform and more or less rapid rotation by means of an electro-motor.

On operating in this way it is found that there is always manifested a current of electricity between two plates of the same metal or between the same conducting substance and a liquid, whether the metal be inoxidizable, like platinum or gold, or oxidizable, like zinc and iron, but of different degrees of strength and in different directions.

With platinum the effect is weak, while with iron and zinc the action is quite energetic. The direction of the current depends on the nature of the substance. Thus an electrode of carbon, platinum, gold, or bismuth takes negative electricity when it is in movement in a conducting liquid, the fixed electrode becoming positively electrified; while the movable electoode of zinc, iron, lead, or antimony takes positive electricity, the fixed plate of the same metal becoming negatively electrified. In these two groups of substances, those which precede are more strongly electrified than those which follow. Copper appears to be at the limit of the two classes of substances, since it gives results very feeble and very variable.

If, with fixed plates, the solution be agitated so that the molecules of liquid be set in motion around one of them, the

effect is the same as when the liquid is motionless and the plate movable.

It appears, therefore, that two plates of the same metal and a conducting liquid may form a couple, provided that one of the plates or the liquid molecules which touch it be in motion. In the case of an oxidizable metal, the plate which is in movement acts as if it were less attacked by the liquid than the fixed plate. On the other hand, with a less oxidizable metal, such as platinum or carbon, the plate in motion acts as if it were more attacked by the liquid than the other plate.

Action of Pulverized Substances mixed with a Liquid Body in which the Metallic Plates are in Motion (Tommasi).—If there be added to the exciting liquid a certain quantity of pulverized material so as to make a thick fluid, the current produced is more or less energetic in accordance with the nature of this substance.

Thus the addition of sand, plumbago, or flowers of sulphur does not increase the energy of the couple, while peroxide of manganese, and especially pulverized carbon previously calcined, augments considerably the electric effects.

If two plates of zinc, one in motion and the other at rest, and an exciting liquid consisting of sodium sulphate be used, a current of certain intensity is obtained which is materially increased by the addition of quite a large quantity of powdered coke to form a thick fluid. The zinc in motion takes positive electricity, and the carbon paste negative. E. M. F. $= 0.123$ volt.

The same effects are obtained by using two plates of platinum depolarized. The plate which rotates takes positive electricity, and the carbon paste negative. There is no current when the movement of rotation ceases.

With a battery composed of ten couples, each consisting of zinc—zinc, sulphate of soda, and carbon paste, and in which the zinc disks are 10 cm. in diameter, it has been found possible to decompose a solution of potassium iodide or copper sulphate, but not acidulated water. From which it appears that

the E. M. F. of this battery should be at least equal to 1.23 volts.

In a zinc platinum couple, in which the movable platinum is in a solution of copper sulphate and separated by a diaphragm from the liquid in which the fixed zinc is located, the electric effect is the same as when the two electrodes are at rest. In this case the depolarization of the platinum plate is obtained by reduction of the copper, and the motion gives no advantage.

When both electrodes of a couple containing different metals are set in motion in their containing liquid, the following effects are observed:

If the electrodes constituting the couple are not attacked by the liquid while at rest, the electric state is *nil*; but as soon as they are set in motion a current is obtained due to the difference of the effects exerted upon them.

Take, for example, the couple carbon—platinum and acidulated water, in the state of rest and after depolarization of the electrodes. This couple gives no current, but as soon as the electrodes in the liquid are set regularly in motion an electric current is produced so directed that the carbon takes negative electricity.

If the electrodes constituting the couple are unequally attacked by the liquid, there is obtained always, by reason of the simultaneous movement of the plates, an increase in the intensity of the current over that which appears when the plates are at rest. In this case the effect produced on the negative plate only is predominant, and it is of no consequence whether the positive plate is at rest or in motion, for depolarization is effected by oxidation of this plate.

The couple having fixed zinc and movable iron electrodes arranged in a paste of carbon and ferrous sulphite in the following table is remarkable, although its electromotive power is low, 0.57 volt, inasmuch as when the cylinder is at rest the deviation of the galvanometer is almost nothing. The results obtained with a movable electrode of iron in a paste of iron peroxide are very nearly the same as those obtained when there is no movement. The E. M. F. of the couple fixed zinc

E. M. F.'S OF COUPLES FORMED WITH AN EXTERIOR ZINC CYL-
INDER IMMERSED IN WATER ACIDULATED TO $\frac{1}{10}$ BY SO_4H_2,
AND A CONDUCTING CYLINDER ENTERING THE POROUS
CUP AND TURNING IN A BODY OF CARBON, SAND, OR
OTHER MATERIAL REDUCED TO A PASTY STATE WITH
A CONDUCTING LIQUID. (E. BECQUEREL, 1854.)

In the Outer Vessel.		In the Porous Cup.		
Metallic Cylinder at Rest.	Liquid, Water acidulated $\frac{1}{10}$ Sulph. Acid.	Metallic Cylinder in Motion (20 revs. per second).	Liquid Paste.	E. M. F. in Volts.
Zinc^{Hg}	Acidul. water	Copper	Fine sand moistened with water acidulated $\frac{1}{10}$.......	0.57
"	"	"	Paste of peroxide of manganese with acidulated water..	1.00
"	"	"	Paste of wood-charcoal and acidulated water..........	0.88
"	"	"	Paste of coke and sodium sulphate....................	0.93
"	"	"	Paste of coke and acidulated water...................	0.99
"	"	"	Same	1.13
"	"	"	Same	0.98
"	"	Platinum	Same	0.79
"	"	Retort-carbon	Same	1.04
"	"	Iron	Paste of coke and ferrous sulphate....................	0.57
"	"	Zinc^{Hg}	Paste of coke and acidulated water...................	0.17
"	"	"	Paste of coke and zinc sulphate............	0.37

and movable platinum in a paste of coke and acidulated water
is three times weaker when the platinum does not rotate. If
the platinum be replaced by copper, the E. M. F. of the couple
in motion is augmented only about one fifth. The E. M. F.
of the couple fixed zinc and movable copper cylinder in a paste
of manganese peroxide and acidulated water decreases one half
when the copper ceases to rotate. If comparison be made of
the quantity of water decomposed by a given cell in accordance
as it is at rest or in motion, it is found that, by reason of the
motion, the effect of the cell is more than seven times greater,
as the following table shows. The battery consisted of ten

couples formed of disks of amalgamated zinc and copper of 10 cm. diameter, carried on a rotary axis. Each couple entered a trough containing an exciting liquid.

Liquid contained.	State of Disks.	Volume of Hydrogen disengaged in 20 minutes.
Water saturated with sodium sulphate	{ At rest	6.25
	{ In motion	46.75
Paste of coke and acidulated water	{ At rest	21.00
	{ In motion	136.00

E. M. F.'s of Certain Couples in Absolute Value.— J. B. Baille (1881) has measured these E. M. F.'s in absolute values in such a way that, the Daniell element being taken as unity, the relation of the other couples to this unit may be very clearly determined by the application of Ohm's laws and transformed into ordinary metric units.

Cell.	Units.	
	C. G. S.	Ordinary.
Volta	0.003281	0.0001048
Copper sulphate (Callaud)	0.002880	0.0000920 maximum.
Daniell	0.003564	0.0001138 average.
Leclanché	0.004438	0.0001417 maximum.
Platinum chloride	0.004830	0.0001542 "
Bunsen	0.006039	0.0001928 average.

The numbers of the second column have been obtained by dividing those of the first by the square root of $g = 980.88$, value of gravity at Paris. They represent a certain mass of electricity; a unit of electric mass being that which, acting upon an equal mass at 1 cm. distance, repels with a force of 1 g.

E. M. F. produced at the Contact of Arterial and Venous Blood, and of each of these Bloods with Different Liquids (Becquerel).—These experiments have been made

with both kinds of blood defibrinated; the arterial blood was placed in a tube closed at one end with parchment-paper, and this, in turn, was disposed in a test-tube containing venous blood. In each of the two bloods was immersed a plate of depolarized platinum.

Positive.*	Negative.	E. M. F.'s.
Arterial blood	Venous blood	0.029
Distilled water	Arterial "	0.161
" "	Venous "	0.194
Venous blood	Bile	0.092
Arterial "	"	0.099
" "	Urine	0.121
Venous "	"	0.095
Grape-juice	Arterial blood	0.123
Sugar and water	" "	0.125
Wine	" "	0.092
Beef-bouillon	" "	0.056
Grape-juice	Venous blood	0.140
Sugar and water	" "	0.145
Wine	" "	0.080
Beef-bouillon	" "	0.044
Distilled water	Artery	0.221
" "	Vein	0.155

The last two experiments were conducted on the living subject.

E. M. F. developed by the " Bony Current."—Becquerel gives the name "bony current" to the electric current observed between two different parts of a bone. The E. M. F. of the bony current, in an animal newly killed, for example, is observed by means of two plates of depolarized platinum, one of which is introduced into the marrow and the other applied to the surface of the bone, the whole being immersed in a vessel of distilled water. The average of several experiments shows that the E. M. F. produced by the bony current is about 0.5 volt.

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* Signs as given by Becquerel.

E. M. F.'s of Contact.—Henkel gives the following table:

Aluminium-zinc.....................0.125 volt.
Zinc-tin..........................0.115 "
   " -cadmium.......................0.120 "
   " -lead..........................0.220 "
   " -antimony......................0.345 "
   " -bismuth.......................0.360 "
   " -mercury.......................0.405 "
   " -iron....... ....0.420 "
   " -copper........................0.500 "
   " -gold..........................0.550 "
   " -silver........................0.590 "
   " -platinum......................0.615 "

According to the experiments of Kohlrausch and Thomson, the E. M. F. of contact of copper and zinc is about equal to 0.5 volt.   According to Pellat, the E. M. F. of contact between zinc and copper may vary between the limits 0.6 and 0.8 volt, according to the physical condition of the metals.   It rarely falls below 0.6 volt unless the metals are highly oxidized.

E. M. F. of Contact (Pellat).

Zinc-silver.......................0.91 volt.
   " -platinum......................0.88 "
   " -gold ....0.85 "
   " -copper........................0.68 "
   " -iron..........................0.56 "
   " -bismuth.......................0.49 "
   " -nickel........................0.47 "
   " -antimony......................0.41 "
   " -tin...........................0.25 "
   " -lead..........................0.15 "

Hoorweg's Law (1880).—If, in a chain formed of different substances, the sum of the electric differences is not zero, a galvanic current is produced.

MEAN CONTACT-DIFFERENCES OF POTENTIAL IN VOLTS: SOLIDS WITH SOLIDS IN AIR. TEMPERATURE 18° C. (AYRTON AND PERRY.)

	Carbon.	Copper.	Iron.	Lead.	Platinum.	Tin.	Zinc.	Zinc^{Hg}.	Brass.
Carbon............	0	.370	.485*	.858	.113	.795	1.096	1.208*	.414*
Copper............	−.370	0	.146	.542	−.238	.456	.750	.894	.087
Iron..............	−.485*	−.146	0	.401*	−.369	.313*	.600	.744*	−.064
Lead..............	−.858	−.542	−.401*	0	−.771	−.099	.210	.357*	−.472
Platinum..........	−.113	.238	.369	.771	0	.690	.981	1.125*	.287
Tin...............	−.795*	−.456	−.313*	.099	−.690	0	.281	.463	−.372
Zinc..............	−1.096	−.750	−.600*	−.210	−.981	−.281	−0	.144	−.679
Zinc^{Hg}.........	−1.208*	−.894	−.744*	−.357*	−1.125*	−.463	−.144	0	−.822*
Brass.............	−.414	−.087	.064	.472	−.287	.372	.679	.822*	0

The numbers without an asterisk were obtained directly by experiment; those with an asterisk by calculation—using the well-known assumption that in a compound circuit of metals all at the same temperature there is no electromotive force.

The numbers in a vertical column below the name of a substance are the differences of potential in volts between that substance and the substance in the same horizontal row as the number, the two substances being in contact. Thus lead is positive to copper, the E. M. F. of contact being 0.542 volt.

The metals were those of commerce, and therefore not chemically pure.

The authors point out that the contact-difference between copper and zinc, which they find to be exactly .750 volt, is a more convenient and reliable standard of E. M. F., when it can be used, than even a Latimer-Clark cell.

Hoorweg divides bodies into two groups:

1. Those in which the conductibility increases with the temperature (dielectrics); and

2. Those in which the conductibility decreases as the temperature increases (adielectrics).

He also formulates the following law:

A current is always produced if the closed chain contains at least one substance belonging to the first group (dielectrics). As the result of a great many experiments, Hoorweg reaches the conclusion that on the contact of metals and insulators, the same as on the contact of dielectric bodies among themselves, there is produced a constant and permanent difference of potential.

E. M. F.'s of Contact deduced from Calorimetric Experiments compared with E. M. F.'s deduced from Electroscopic Measurements. (Pellat, 1880.)

	According to Calorimetric Measurements.	According to Electroscopic Measurements.
Copper-iron.	+ 0.0029 volt.	+ 0.13 volt.
" -cadmium	+ 0.0005 "	+ 0.61 "
" -zinc..	+ 0.0004 "	+ 0.80 "
" -bismuth........	− 0.0219 "	+ 0.22 "
" -antimony.	+ 0.0055 "	+ 0.25 "

It will be apparent from the foregoing that there is no relation either between the relative values or the absolute magnitudes and the numbers obtained by these two modes of measurement. Even the signs may differ. One of the two methods is therefore to be rejected.

The numbers of the first column are deduced from experiments as made on the Peltier phenomenon by Leroux; they agree with the relative measurements given by Edlund and with an absolute determination for the zinc-iron couple by Bellati.

The difference which is observed in the table is due, according to Pellat, to the fact that the calorific phenomenon observed by Peltier corresponds to the *difference* between the

work of the two forces (closely approximating in absolute magnitude) and not to the work of the electric forces only, as is premised in order to deduce the E. M. F.'s of contact.

This explains why the calorimetric measurements give numbers from 500 to 1000 times less than the electroscopic measurements.

Difference of Potential of the Electric Coatings (Couches Electriques) *which cover Two Metals in Contact* (Pellat, 1881). —1. Two different metals connected metallically are covered when in the state of equilibrium with electric coatings having unequal potentials.

2. This difference of potential depends only on the nature of the most superficial layer on the metal. It changes materially when the surface is mechanically hardened.

In this case the latter becomes almost always positive.

The superficial hardening diminishing spontaneously and disappearing in time, the potential difference returns to its first value. It is independent of whether the surface be polished or unpolished. Traces of foreign substances, forming a coating the thickness of which is so small as to be invisible, suffice profoundly to modify its value.

3. It depends on temperature, a hot portion and a cold portion of the same metal acting like two dissimilar metals.

4. The pressure or the nature of a gas surrounding the metals has a clear but very weak influence on its value. The variations of potential difference are always behind the variations of pressure or of nature of the gas which provoke them; they are only an indirect consequence due to the light modification caused on the metallic surfaces; the value of the potential difference appears to be, in fact, independent of the gaseous dielectric.

5. The difference of potential betwen the electric coatings which cover two metals connected metallically has the same value as the electromotive force of a single-liquid cell containing these two metals, provided the E. M. F. be determined before any alteration of the metallic surfaces immersed in the liquid occurs; these alterations are produced very rapidly.

This amounts to the same thing as saying that the E. M. F. of a cell formed of two metals and one liquid (alcohol) has the same value as the difference of potential of the electric coatings which cover two metals in contact in air.

All the experiments made by Pellat confirm this law. They were performed on the following metals: copper, brass, zinc, lead, silver, antimony.

6. It is extremely probable that the difference of potential observed between the electric coatings which cover two metals connected metallically represents the difference of potential which exists between these metals.

No reason, theoretical or experimental, can be invoked against the existence of a difference of potential between two metals in contact.

7. This last quantity has no relation to the thermo-electric E. M. F. measured by the Peltier phenomenon.

8. It has only a vague and distant relation to the difference of oxidizability of the metals.

Origin of the Electricity developed at the Contact of Two Different Metals.—Exner (1880) has been led, by his researches on polarization, to consider that the electricity developed at the contact of two metals is due to the difference of chemical action exerted by the surrounding medium upon these two metals, and that this quantity of electricity is proportional to the heat of oxidation of the metal, as in hydro-electric couples.

The numerical values have been calculated by the author by dividing half of the heat of combustion of the metal by the calorific value of the Daniell element.

	Observed.	Calculated.
Zinc-platinum	0.881 Daniell.	0.879 Daniell.
Copper-platinum	0.367 "	0.383 "
Iron-platinum	0.704 "	0.701 "
Silver-platinum	0.083 "	0.062 "

The difficulty of measuring this last quantity permits these results to be considered as satisfactory.

In order to study the influence of different mediums on two

plates of the same metal, two plates of silver are used, one of which is arranged in a glass tube in which circulates a current of chlorine, and the other is in contact with the air. The values are as follows:

Observed.......................... ....0.543
Calculated 0.540

The disengagement of electricity begins and ends at the same time as the action of the chlorine.

TABLE SHOWING DIFFERENCE OF POTENTIAL OF ELECTRIC COATINGS WHICH COVER LIQUIDS AT CONTACT. (E. BI- CHAT AND R. BLONDLOT, 1883.)

Platinum electrodes. Normal solution of sodium sulphate (1 part by weight of sodium sulphate and 24 parts of water). Temperature, 12° to 18° C.

Water acidulated with $\frac{1}{10}$ its vol. of sulphuric acid.
Normal solution of sodium sulphate.... − 0.146 volt.
Ordinary nitric acid.
Normal solution of sodium sulphate.... − 0.677   "
Ordinary nitric acid.
Water and $\frac{1}{10}$ its vol. of sulphuric acid. − 0.544   "
Pure commercial hydrochloric acid.
Normal solution of sodium sulphate.... − 0.575   "
Potash solution (100 grams pure potash, 500 water).
Normal solution of sodium sulphate.... + 0.052   "
Potash solution (300 grams pure potash, 500 water).
Normal solution of sodium sulphate.... + 0.154   "
Zinc sulphate solution (300 grams pure zinc sulphate, 900 water).
Normal solution of sodium sulphate.... none perceptible.
Saturated solution of copper sulphate.
Normal solution of sodium sulphate.... none perceptible.
Solution of zinc sulphate (300 grams pure zinc sulphate, 900 water).
Saturated solution of copper sulphate.. none perceptible.
Normal solution of sodium sulphate with addition of 0.0003 chromic acid.
Normal solution of sodium sulphate.... none perceptible.

Solution of sodium hyposulphite (100 *grams of sodium hypo-sulphite*, 500 *water*).

Normal solution of sodium sulphate.... none perceptible.

Solution of sodium sulphate (100 *grams of pure sodium sulphate*, 150 *water*).

Normal solution of sodium sulphate (100
grams sod. sulph., 2400 water) .... — 0.013 volt.

It will be seen that the acids and potash in relation to the sodium sulphate solution give results with contrary signs.

AVERAGES IN VOLTS OF THE POTENTIAL DIFFERENCES AT CONTACT OF SOLIDS WITH LIQUIDS, AND OF LIQUIDS WITH LIQUIDS IN AIR. (AYRTON AND PERRY.)

[All the liquids and salts used were chemically pure. The solids, on the contrary, were only commercially pure. The numbers opposite the substances are the differences in potential in volts between each substance and the substance named at the head of the table. Thus platinum is positive in relation to mercury, and the difference of potential due to the contact is 0.156 volt. Platinum is equally positive in relation to distilled water, but the difference of potential is from 0.285 to 0.345.]

Average temperature, 16° C.

Mercury.

Carbon	0.092	volt.
Copper	0.308	"
Iron...............	0.502	"
Platinum..............................	0.156	"

Distilled Water.

Carbon............. .... 0.01	to 0.17	volt.
Copper....................... 0.269	to 0.100	"
Iron.................................	0.148	"
Lead	0.171	"
Platinum.............. .... 0.285	to 0.345	"
Tin.................................	0.177	"
Zinc...................... — 0.105	to + 0.156	"
Zinc^{Hg}..............................	0.100	"
Brass...........................	0.231	"
Sat. sol. copper sulph. at 15°	0.043	"
Sat. sol. zinc sulph. at 15°............	0.164	"

Saturated Solution of Alum at 16°.5.

Copper...............................	− 0.127 volt.
Iron................................	− 0.653 "
Lead................................	− 0.139 "
Platinum............................	− 0.246 "
Tin.................................	− 0.225 "
Zinc................................	− 0.536 "
Brass...............................	− 0.014 "

Saturated Solution of Copper Sulphate at 15°.

Copper.............................	0.070 volt.
Distilled water......................	− 0.043 "
Sat. sol. zinc sulph. at 15°.3...........	+ 0.095 "
1 part distilled water and 3 parts sat. sol. zinc sulph..................	0.102 "

Solution of Copper Sulphate. D. = 1.087 at 16°.6.

Copper.............................	0.103 volt.
Sol. zinc. sulph. D. = 1.125 at 16°.9 ..	0 090 "

Solution of Sodium Chloride. D. = 1.18 at 20°.5.

Copper.............................	− 0.475 volt.
Iron................................	− 0.605 "
Lead................................	− 0.267 "
Platinum............................	− 0.856 "
Tin.................................	− 0.234 "
Zinc................................	− 0.565 "
Brass...............................	− 0.435 "

Sat. Solution of Ammonium Chloride at 15°.5.

Copper.............................	− 0.396 volt.
Iron................................	− 0.652 "
Lead................................	− 0.189 "
Platinum............................	− 0.057 " (− ?)
Tin.................................	− 0.364 "
Zinc................................	− 0.637 "
Brass...............................	− 0.348 "

Saturated Solution of Zinc Sulphate at 15°.3.

Zinc.................................. — 0.430 volt.
Zinc^{Hg}.............................. — 0.284 "
Distilled Water................... ... — 0.164 "
Sat. sol. copper sulph. at 15°.......... — 0.095 "

Solution of Zinc Sulphate. D. = 1.125 *at* 16°.9.

Zinc.................................. — 0.238 volt.

Mixture of Dist. Water 1 *part and Sat. Sol. Zinc Sulphate* 1 *part.*

Sat. sol. copper sulphate at 15° .... — 0.093 volt.

Mixture of Dist. Water 1 *part and Sat. Sol. Zinc Sulphate* 3 *parts.*

Zinc .... — 0.444 volt.
Sat. sol. copper sulph. at 15°......... — 0.102 "

Distilled Water with a small trace of Sulphuric Acid.

Zinc .... — 0.241 volt.

Distilled Water with $\frac{1}{5}$ *per cent of Sulphuric Acid.*

Zinc .... — 0.289 volt.

Distilled Water with $\frac{1}{2}$ *per cent of Sulphuric Acid.*

Zinc................................. — 0.312 volt.

Mixture of 200 *grams Dist. Water and* 10 *grams Concen. Sulph. Acid.*

Zinc .... — 0.344 volt.

Mixture of 100 *c.cm. Dist. Water and* 10 *c.cm Conc. Sulph. Acid.*

Carbon .... — 0.035 volt, about.
Zinc^{Hg} .... — 0.358 "

Mixture of 50 *grams Distilled Water and* 10 *grams Concen. Sulph. Acid.*

Zinc^{Hg} .... — 0.429 volt.

Mixture of 100 grams Distilled Water and 500 grams Concen. Sulph. Acid.

Carbon	+ 0.01 to 0.3	volt.
Lead	− 0.120	"
Tin	− 0.250	"
Brass	+ 0.016	"

Concentrated Sulphuric Acid.

Carbon	0.55 to 0.85	volt.
Copper	1.113	"
Lead	0.720 to 1.252	"
Platinum	1.600 to 1.300	"
Zinc^{Hg}	0.848	"
Distilled water	1.298	"
Sat. sol. alum. at $16°.5$	1.456	"
Sat. sol. copper sulph. at $15°$	1.269	"
Sat. sol. zinc sulph. at $16°.9$. $D. = 1.25$	1.699	"

Concentrated Nitric Acid.

Platinum .... 0.672 volt.

Paste of Mercurous Sulphate.

Mercury .... 0.475 volt.

The preceding tables enable the E. M. F.'s of the ordinary couples to be calculated by simply taking the algebraic sum of the potential differences at the various contacts. Thus :

Daniell Element.

Copper and sat. sol. copper sulphate	+ 0.070
Sat. sol. copper sulph. and sat. sol. zinc sulph.	− 0.095
Sat. sol. zinc sulphate and zinc	+ 0.430
Zinc and copper.	+ 0.750

<div align="right">

1.155 volts.

</div>

Grove Element.

Copper and platinum........................ +0.238
Platinum and strong nitric acid............ +0.672
Strong nitric acid and very dilute sulph. acid + 0.078
Very dilute sulph. acid and zinc........... + 0.241
Zinc and copper............................ + 0.750

———————

1.979 volts.

Becquerel (1870) (contrary to the opinion of many physicists) has remarked that when platinum and gold are completely depolarized by taking the necessary precautions, they yield no current when they are placed in distilled water.

Influence of Pressure on the Electric Difference between a Liquid and a Metal in Contact.   (E. Bichat and R. Blondlot, 1883.)

Nature of the Couple.	Pressure.	E. M. F.'s.
Copper–platinum, copper sulphate......100 atmos.		0.001 volt.
Silver–platinum–silver nitrate..........	"	0.0005 "
Copper–platinum–water..............	"	0
Silver–platinum–water	"	0

The values of the third column show the increase of E. M. F. of the couple due to pressure of 100 atmospheres above normal atmospheric pressure.

CHAPTER XIX.

GENERAL PRACTICAL DATA. (*Continued.*)

POLARIZATION.

Polarization by Hydrogen. (Raoult, 1863).—The Smee element operating alone appears to be the most suitable for the study of polarization by hydrogen. In order to secure greater constancy, the metals were separated by a porous partition, and at every experiment the acid on the platinum side was renewed.

I. *Effect of Air contained in Water.*

Positive Electrode.	Negative Electrode.	E .M. F.
Zinc^{Hg} in $\frac{1}{10}$ sulphuric acid solution	Platinum in sulphuric acid diluted with 10 times its weight of water and exposed to air for 2 days..................	0.74 volt.
Same	Platinum in same sulph. acid solution deprived of air by boiling...........	0.64 "
Same	Platinum in same sulph. acid solution charged with hydrogen............... ...	0.63 "

II. *Effect of Impurities.*

Positive Electrode.	Negative Electrode.	E. M. F.
Zinc^{Hg} in $\frac{1}{10}$ sulphuric acid solution	Platinum in sulphuric acid diluted with 10 times its weight of water boiled :	
	At the beginning of the action......	0.64 volt.
Same	After 15 minutes...................	0.63 "

* Raoult's terms reversed to accord with definitions of this book.

Positive Electrode.	Negative Electrode.	E. M. F.
Zinc^{Hg} in $\frac{1}{10}$ sulphuric acid Solution	Platinum in sulphuric acid solution as above, to which is added $\frac{1}{4}$ of its volume of concentrated zinc sulphate :	
	At the beginning of the action.....	0.62 volt.
Same	After 15 minutes	0.37 "
Same	" 30 "	0.53 "
Same	Platinum in sulphuric acid solution as above, containing barely perceptible traces of copper sulphate :	
	At the beginning of the action......	0.61 "
Same	After 15 minutes	0.56 "
Same	" 30 "	0.56 "

In all these experiments the development of hydrogen is rapid.

III. *Effect of Degree of Concentration of the Acid.*

Positive Electrode.	Negative Electrode.	E M. F.
Zin ^{Hg} in $\frac{1}{10}$ sol. sulph. acid	Platinum in $\frac{1}{10}$ sol. sulph. acid.....0.64 volt.	
" " $\frac{1}{100}$ " "	" " " " " .....0.65 "	
" " $\frac{1}{10}$ " "	" " $\frac{1}{100}$ " " .....0.62 "	

IV. *Effect of Temperature.*

	Zinc-platinum. (Smee Couple.)	Zinc-copper. (Wollaston Couple.)
10°	0.66 volt.	0.56 volt.
40°	0.68 "	0.62 "
80°	0.72 "	0.70 "
100°.................	0.74 " (?)*	0.73 " (?)*

V. *Effect of Current Intensity.*—Polarization by hydrogen increases with the intensity of the current, but only up to a certain limit which it does not exceed and which corresponds to a very marked yielding of gas.

VI. *Effect of Platinum Cells.*—When the platinum surface is increased with relation to that of the zinc, E. M. F. augments. This augmentation is in inverse ratio to the quantity of gas yielded per minute and per square centimetre.

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* At the boiling temperature the E. M. F. is variable.

VII. *Effect of the Movement of the Platinum.*—When the platinum is agitated and the disengagement of hydrogen is large, the E. M. F. in an aerated liquid increases, but it does not vary in a liquid free from air. This fact has also been observed by Joule.

VIII. *Effect of the Acid surrounding the Negative Electrode.*—The polarization of platinum by hydrogen remains very nearly the same in different acids.

IX. *Effect of the Condition of the Surface and of the Nature of the Negative Electrode.*—In the following table the metals of the negative electrode are immersed in $\frac{1}{10}$ solution of sulphuric acid deprived of air.

Positive Electrode.	Negative Electrode.	E. M. F.'s. Before Polariz.	After Polariz.
Zinc^{Hg} in sulph. acid $\frac{1}{10}$	Polished platinum.....	1.66	0.63
"	Scratched "	1.63	0.64
"	Platinized "	1.65	0.63
"	" silver.......	1.50	0.60
"	Gold..............	1.64	0.57
"	Polished copper.......	1.00	0.55
"	Scratched "	1.00	0.56
"	Electrol. rough copper	0.99	0.56
"	Iron................	0.61	0.53
"	Amalg. copper........	1.03	0.032
"	Mercury............	1.18	0.010

Comparative Table showing Values found for the Polarization of Hydrogen by Various Authors.

	Polarization by Hydrogen. *L. S.	B.	R.
Platinum	1.56 volt.	0.82 volt.	1.03 volt.
Gold..............	1.56 "	0.90 "	1.07 "
Copper	0.97 "	0.50 "	0.45 "
Mercury	1.88 "	0.74 "	1.17 "

*(L. S.) Lentz and Saweljev. (B.) E. Becquerel. (R.) Raoult. The values obtained by Raoult are the differences between the figures of the preceding table.

Polarization by Chlorine. (Raoult, 1863.)

Positive Electrode.	Negative Electrode.	—E. M. F.'s.—	
		During Polariz. volts.	Before Polariz. volts
Zinc in conc. zinc chloride	Platinum in pure conc. HCl.........	1.84	1.48
"	Platinum in HCl. sat. with chlorine......	2.15	1.95
"	Carbon...............	2.21	1.95
Copper, copper chloride	"	1.15	0.88
" " sulphate	"	1.12	0.84

+

Platinum, pure HCl

—

Platinum covered with gaseous Cl and chlorated HCl $\Big\}$ 0.37

Polarization of Electrodes by Chlorine and Hydrogen. (D. Maccaluso, 1874.)

I. *Polarization by Chlorine.*—1. The E. M. F. which is de‐
veloped between two plates of platinum placed, one in pure
hydrochloric acid and the other in hydrochloric acid containing
free chlorine, is not constant, but increases gradually with time
up to a maximum.

2. This E. M. F. increases with the quantity of free
chlorine up to a determinate value, about 0.67 volt, which it
rarely passes.

3. If the immersion of the platinum plate in the acid so‐
lution precedes the addition of the chlorine, the E. M. F.
increases rapidly from the time that this addition begins; it
increases very nearly proportionately to the quantity of chlo‐
rine added, and tends gradually to a maximum.

4. If, on the contrary, the platinum plate is placed in a
solution already containing chlorine, the E. M. F. increases at
first but slowly on the addition of the first drops of chlorine

solution, and it is only little by little that the increase of
E. M. F. follows the rate set forth in paragraph 3.

5. The chlorine developed on a platinum plate by the
galvanic current has a negative E. M. F. more marked than
has chlorine prepared by the ordinary process.

6. The E. M. F. developed between a platinum plate
charged with this active chlorine and another charged with
ordinary chlorine is at least equal to 0.5 volt, while the E. M. F.
which is manifested between a plate charged with ordinary
chlorine and a plate of pure platinum entering hydrochloric
acid is equal to 0.67 volt.

7. Polarization of electrolytic chlorine attains more rapidly
a maximum in dilute solutions of hydrochloric acid than in
concentrated solutions, but in very dilute solutions the abso-
lute value of this maximum is independent of the degree of
concentration.   Too high a degree of concentration prevents
polarization by electrolytic chlorine from attaining this maxi-
mum.

8. In concentrated hydrochloric acid polarization by elec-
trolytic chlorine diminishes more rapidly after the interruption
of the polarizing current than in dilute acid.   The presence
of a greater quantity of hydrochloric acid determines a more
rapid return of the active chlorine to the state of ordinary
chlorine.

9. On an elevation of temperature comprised between 17°
and 100° C. polarization of platinum charged with ordinary
chlorine diminishes by a quantity of 0.607 volt only, while
between 16° and 93° the polarization of platinum charged
with active chlorine undergoes a diminution much greater and
equal to 0.484 volt.

II. *Polarization by Hydrogen.*—The E. M. F. which is
developed between two plates of platinum both immersed in
hydrochloric acid and one of which is pure, the other being
charged with hydrogen chemically produced, varies between
0.67 volt and 0.75 volt, according to the degree of concentra-
tion of the acid.   It is the less as the acid is more concentrated.

This E. M. F. is much greater when the hydrogen con-densed at the surface of the electrode has been obtained electrolytically. It then reaches 1.01 instead of 0.73 volt. A too high degree of concentration of the hydrochloric solution hinders the formation of the active hydrogen which produces this greater E. M. F.

Similar results are obtained by using carbon electrodes instead of platinum electrodes, only in this case the polarization tends to a maximum immediately after the closing of the electrolyzing current.

Polarization by Oxygen (Raoult).—The electrolyte is a concentrated solution of copper sulphate; the positive* electrode is a large plate of copper, and the negative electrode a platinum wire of 1 sq. cm. surface; the decomposing cell is of the Bunsen type.

Effect of Time.

No. of Elements.	Development of Oxygen.	E. M. F.'s after			
		1 Min.	5 Min.	15 Min.	1 Hour.
1	Very weak...	0.980	1.01	1.08	1.15 volts.
2	Strong......	1.26	1.78	1.79	1.80 "
5	Very strong..	1.77	1.78	1.80	1.80 "
10	Tumultuous	1.78	1.79	1.78	1.76 "

If the negative electrode is placed in a small porous cup, the polarization further increases.

Effect of Temperature.

No. of Elements.	Temp. of Electrolyte.	E. M. F.'s.
5	80°	1.41 volts.
5	60°	1.53 "
5	40°	1.66 "
5	20°	1.76 "
5	10°	1.78 "

---

* Raoult's terms reversed to accord with definitions of this book.

It appears, therefore, that the polarization of the platinum by oxygen diminishes considerably as the temperature increases. This diminution takes place similarly in copper nitrate : it is about 0.05 volt per degree centigrade.

Effect of the Area of the Negative Electrode.

Immersed Surface of the Platinum.	Approximate Quantity of Oxygen developed per sq. cm.	E. M. F.'s.
28 sq. cm.	0.1 c. cm.	1.51 volts.
14 "	0.2 "	1.60 "
7 "	0.3 "	1.71 "
1 "	1 "	1.80 "
0.1 "	5 "	1.77 "

When the development of oxygen is very rapid the polarization of the negative electrode varies but little with its dimensions.

Effect of Current Intensity.

The negative electrode being a platinum wire of 1 sq. cm. of surface, we have :

Temp. of the Copper Sulphate.	No. of Elements.	C. cm. of Oxygen developed per Minute.	E. M. F.'s.
7°	1	Very small	1 volt.
7°	2	0.4 c. cm.	1.60 "
7°	4	0.6 "	1.78 "
9°	10	1.7 "	1.79 "
15°	20	3.1 "	1.75 "

Thus polarization by oxygen increases with the number of elements until the gas disengaged reaches about ½ c. cm. per minute and per square centimetre.

Effect of the State of the Platinum Surface.

No. of Elements.	Polished Plate.	Rough Plate.	Platinized Plate.
1	0.97 volt.	0.93 volt.	0.99 volt.
2	1.75 "	1.73 "	1.73 "
5	1.78 "	1.78 "	1.78 "
10	1.76 "	1.78 "	1.78 "

From which it appears that the maximum polarization is independent of the extent of platinum surface.

Effect of the Nature of the Negative Electrode.

Metal polarized by Oxygen.	E. M. F., Maximum.
Platinum....................	1.78 volts.
Carbon	1.73 "
Gold	1.83 "

Effect of Motion of the Negative Electrode.—If the platinum be agitated, the polarization decreases ; the diminution is greater as the development of gas is less.

Effect of the Nature of the Liquid in which the Positive Electrode is immersed.—The negative electrode is a platinum wire in a small porous cup filled with concentrated copper sulphate ; the positive electrode is a large plate of metal in a reducible salt of the same metal. The current is obtained from three Bunsen elements.

Negative Electrode.	Positive Electrode.	Max. E. M. F.
Platinum covered with oxygen in conc. copper sulphate	Silver nitrate, silver	1.35 volts.
Same	Copper nitrate, copper............	1.72 "
Same	Copper sulphate, "	1.78 "
Same	Lead acetate, lead	2.27 "
Same	Zinc sulphate, zinc...............	2.23 "
Same	Concentrated nitric acid, platinum	1.06 "

Effect of the Liquid in which the Negative Electrode is immersed.

The electrolyte is divided by a porous diaphragm. On one side is a plate of copper in copper sulphate, on the other a platinum wire in various solutions.

Positive Electrode.	Negative Electrode.	⌐E. M. F.'s.⌐ Before Polariz. volt.	During Polariz. volt.
·Copper in concen. copper sulphate	Platinum in concentrated copper nitrate...	0.45	1.83
Same	Same, diluted with 7 volumes of water....	0.43	1.80
Same	Concentrated copper sulphate	0.30	1.78
Same	Same, after 1 day's development of oxygen	1.08	1.83
Same	Concen. copper sulphate + 7 vol. of water	0.30	1.70
Same	Concentrated zinc sulphate...............	0.20	1.82
Same	Concentrated potassium sulphate.........	0.086	1.78
Same	Concentrated sulphuric acid..............	0.086	2.05
Same	Sulphuric acid + 10 volumes water.......	0.54	1.78
Same	Same, after 1 day's development of oxygen	1.24	1.83
Same	Sulphuric acid + 500 volumes water	0.48	1.66
Same	Concentrated nitric acid	0.83	1.80
Same	Nitric acid + 5 volumes water............	0.70	1.81
Same	Potash in 12 times its weight of water....	0.19	0.95

Polarization by Ozone.—Schoenbein (1840) has observed that plates of platinum or gold submitted to the action of ·ozone become very strongly polarized, in fact so much so as to be negative to other plates previously placed in pure oxygen. The oxidizable metals, copper excepted, do not show this ·effect.

Change which takes place on the Surface of a Metal during its Polarization by Oxygen or Hydrogen.—R. Koch (1879) has observed that when platinum rubs against glass under acidulated water it suffices to connect the platinum to the positive pole (terminal) of the cell to polarize it by hydrogen, and thus to augment the friction. The same thing is true of palladium. In the case of platinum it is found that the friction is two or three times increased by the effect of polarization. Eighteen-carat gold gave no results.

Krouchkoll (1880) has found that polarization by hydrogen acts in a direction opposite to that by oxygen.

K. Waitz (1883), using plates of platinum, nickel, and gold immersed in various solutions, saline, acid, or alkaline, has observed that in general polarization by hydrogen diminishes friction,* while polarization by oxygen increases it, and that

---

* Experiments have frequently been made to reduce skin friction of bodies moving in water by producing on the surfaces electrolytic hydrogen.

friction varies continuously with the E. M. F. of polarization. This variation in friction is not due to the fact that gases are disengaged on the platinum surface, for the phenomenon takes place when the E. M. F. is too small (0.03 to 0.49 volt) to decompose the electrolyte. Neither does it appear to be due to the occlusion of gas in the metal, for the duration of the polarization is immaterial.

Waitz has also observed that the coefficient of friction between the water and the metal is not altered by the polarization of the metallic plate.

Polarization of Electrodes.—Laws of Lenz and Saweljev:

1. The polarization of plates which act as electrodes does not take place except when gases are disengaged on their surfaces.

2. The polarization which results from the decomposition of a liquid between two electrodes is the sum of the polarization produced on each electrode.

3. The polarization and electromotive forces in each cell in a circuit where decomposition takes place are to be added together with reference to the sign depending upon the direction in which it acts.

E. M. F.'S OF POLARIZATION (ARBITRARY UNIT).

[The unit of current here is that current which deviates the galvanometer needle one degree; the unit of resistance, one turn of the rheostat; the unit of E. M. F., that which produces the current 1 through the resistance 1.]

Platinum in oxygen	....	2.49
" " chlorine	....	0.00
Graphite " oxygen	....	1.33
Gold " "	....	2.71
Platinum " hydrogen	....	3.67
Zinc " "	....	0.90
Copper " "	....	2.30
Tin " "	....	1.55
Iron . " "	....	0.48
Mercury " "	....	4.37
Copper " oxygen	....	0.69

Polarization of Platinum in Water.—The E. M. F. of polarization increases with that of the principal current up to a certain maximum the value of which, according to different authors, lies between 1.6 and 2.7 volts.

According to F. Exner (1878), if Wollaston electrodes and distilled water perfectly free from air be used, it is easily seen that the E. M. F. of polarization is constantly equal to the E. M. F. of the primary current up to the point when this last is equivalent to 2.19 volts. From this point onward, however, the E. M. F. of polarization remains constant while the intensity of the primary current increases.

With the same Wollaston electrodes and acidulated water the maximum is perceptibly the same as before (2.22 volts); but it is obtained only with a much greater intensity of the primary current. The same is true when the Wollaston electrodes are replaced by platinum plates. In this case the maximum is less, being only 2.062 volts. In the same circumstances the E. M. F. of polarization, which was 2.062 volts for water free from air, falls to 1.54 volts when the water contains air in solution.

According to Wiedemann (1855), different opinions rendered by physicists on the polarity of the electrodes may all be referred to two fundamental principles: first, chemical action; second, a special electric condition which solid or liquid conductors assume under the influence of currents—a state which they keep when the current has been interrupted. It appears well demonstrated that if the polarity of electrodes is the necessary consequence of an electric current, it does not always indicate a chemical decomposition.

Transmission of Current in Water when the Dimensions of the Platinum Electrodes are not Equal (Slouguinoff, 1880).— Two platinum electrodes, one a wire and the other a plate 64 sq. cm., were placed in water acidulated with a few drops of sulphuric acid. When the current moved from the wire to the plate in the liquid, its intensity appeared to be greater than when moving in the opposite direction. This phenomenon depends on the variation of the E. M. F. of polarization, and

proves that the polarization is less considerable when hydrogen is disengaged on the plate. Consequently when the surface of the plates increases, the E. M. F. of polarization by hydrogen decreases much more than that by oxygen.

Two platinum plates polarized by hydrogen and immersed in acidulated water produce a current the direction of which changes several times.

Two plates charged with oxygen produce a current invariable in direction but of very brief duration.

Effect of Water in Agitation along the Polarized Surfaces of Platinum (H. Helmholtz, 1881).—It is necessary to distinguish between the primary current and the current of agitation. According as the agitated electrode is cathode or anode to the current, the latter is called " cathodic" or " anodic."

1. With a strong, primary, cathodic current the current of agitation is in the same direction.

2. With weak, primary, anodic or cathodic currents the currents of agitation are anodic with one exception.

3. Charging by hydrogen of the superficial coatings of the platinum favors in general the anodic direction.

4. Between two electrodes similarly treated anodic agitation currents are generally produced.

These agitation currents are not due to acceleration of the modifications produced by polarization. Saving the complication due to changes in resistance, an electrode rich in hydrogen gives cathodic agitation currents; an electrode moderately charged gives strong anodic currents, and an electrode weak in hydrogen weak anodic currents.

Polarization of certain Metals (Slouguinoff, 1878).—A single polarizing Poggendorff cell produces a polarization of aluminium electrodes of 1.243 volts; four cells, a polarization of 4.147 volts; and eight cells, 7.06 volts. The E. M. F. of polarization of bismuth is 1.425 volts with one Poggendorff cell, 4.752 volts with four cells, and 7.992 volts with seven cells.

Slouguinoff has also determined the maximum E. M. F. of the following bodies :

Electrolytic copper............... 0.56 volt.
Cadmium .... 0.13   "
Carbon .... 2.46   "
Lead .... 2.59   "

F. Kohlrausch has experimentally demonstrated that alternating currents do not produce any polarization in an electrolytic cell, provided the electrodes are sufficiently large. This fact has enabled E. Cohn (1881) to measure the resistance of a small cell polarized by a constant current. He finds that polarization by hydrogen augments the resistance, while polarization by oxygen diminishes it. These variations in resistance, however, are so small that they may be neglected in the majority of experiments.

Polarization of Electrodes composed of Different Metals in Different Solutions. (Latimer Clark.)

Metallic Electrodes.	Liquid.		E. M. F.	
Platinum	Sulphuric acid, 6% dilution		2.72	volts.
"	Nitric	"	1.23	"
Copper	Sulphuric	"	1.08	"
Zinc	"	"	0.723	"
Retort-carbon	Nitric	"	0.626	"
Zinc^{Hg}	Sulphuric	"	0.453	"
Iron	"	"	0.162	"

Polarization of Mercury Electrodes during Electrolysis of Mercurous Nitrate.—Slouguinoff (1877) has found that the maximum E. M. F. of polarization of the anode with relation to non-polarized mercury is 0.03 volt; that of the cathode, 0.028 volt. The polarization of the cathode with relation to the anode is 0.058 volt, exactly the sum (0.028 + 0.03) of the two numbers already cited. Concentration of the solution has little influence on this phenomenon, but the nitrate crystals which tend to cover the anode with a resisting crust aid in augmenting the polarization.

Remanent Polarization.—This term has been proposed by D. Tommasi. Whenever a certain number of discharges,

direct or induced, all in the same direction, have traversed a voltmeter, if a series of discharges exactly equal to the preceding, but in opposite direction, be established, the currents of polarization are less intense in the second series of experiments than in the first.

Thus two plates of platinum or of gold placed in a decomposable liquid and which are polarized several times in the same way possess a tendency to become polarized anew in the same direction.

This fact was first observed by Saweljev and subsequently carefully studied by Verdet (1848).

On the Depolarization of Electrodes by Solutions.—In order that an electrode may be depolarized it is necessary that it should be formed of the metal which is contained in the solution.

SPONTANEOUS POLARIZATION IN OXIDIZING LIQUIDS.
(RAOULT, 1863.)

Elements.		Time of Immersion of the Platinum or Gold.	E. M. F.'s.
Positive Electrode.*	Negative Electrode.		
			volt.
Copper in conc. copper sulphate	Platinum in nitric acid (acid 1, water 5)	6 s. 1 m. 3 m. 20 m.	0.68 0.70 0.72 0.74
Same	Gold in nitric acid (acid 1, water 20)	10 s. 1 m. 8 m. 20 m.	0.45 0.51 0.57 0.62
Same	Platinum, chloride of platinum (chloride 1, water 1000)	2 s. 1 m. 5 m.	0.62 0.63 0.64
Same	Platinum, chromic acid (acid 1, water 10)	20 s. 1 m. 3 m.	0.85 0.90 0.91
Same	Gold, chromic acid (acid 1, water 10)	20 s. 1 m. 1 m.	0.86 0.89 0.89

* Raoult's signs reversed.

Thus copper is the only metal which is depolarized in copper sulphate, while gold, silver, and platinum become polarized in that solution. Inversely, copper polarizes in sulphate of zinc, cobalt, etc. A salt depolarizes only its own metal. For the same reason a couple formed of plates of copper and platinum immersed in copper sulphate furnish a current but of short duration; the platinum taking, owing to polarization, an E. M. F. equal and contrary to that of the copper. It is possible to go even further and to communicate to the platinum by means of an exterior battery a higher electromotive force ($\frac{1}{36}$ Daniell) than that of copper; so that thereupon the platinum acts like a metal more oxidizable than copper.

SPONTANEOUS POLARIZATION IN REDUCING LIQUIDS
(RAOULT, 1863.)

Elements.		Time of Immersion of the Platinum or Gold.	E. M. F.'s.
Positive Electrode.*	Negative Electrode.		
			volt.
Copper in copper sulphate	Platinum, hyposulphite of sodium (hypos. 1, water 5)	6 s. 1 m. 5 m.	0.12 0.22 0.23
Same	Gold, hyposulphite of sodium (hypos. 1, water 5)	6 s. 1 m. 5 m.	0.25 0.29 0.34
Same	Platinum, cyanide of potassium (cyan. 1, water 10)	10 s. 1 m. 3 m. 10 m.	0.23 0.28 0.39 0.41
Same	Gold, cyanide of potassium (cyan. 1, water 10)	10 s. 3 m. 6 m.	0.76 0.90 0.91
Platinum in dilute sulph. acid saturated with hydr.	Copper, copper sulphate.	1 s. 5 s. 20 s.	0.33 0.13 0.01
	After this, the E. M. F. changes direction.		
Copper in copper sulphate	Platinum, sulph. acid $\frac{1}{10}$ saturated with hydrogen.	1 m. 2 m.	0.04 0.09

* Raoult's signs reversed.

Similar experiments have been made by Lippmann (1879) with plates and solutions of silver, mercury, lead, cobalt, and zinc. The accuracy of these results, however, is contested by Maccaluso, who claims to have found that copper electrodes are depolarized almost as rapidly in a solution of pure zinc sulphate as in the same solution to which a small quantity of copper sulphate is added. With regard to cobalt he finds that the metal polarizes in its own solution the same as in solutions of foreign metals.

SPONTANEOUS POLARIZATION IN LIQUIDS NEITHER OXIDIZ-
ING NOR REDUCING. (RAOULT, 1863.)

Elements.		Time of Immer- sion.	E. M. F. in Volts.	
Positive Electrode.*	Negative Electrode.		Platinum.	Gold.
Copper in copper sulphate.	Platinum or gold in sulphuric acid $\frac{1}{10}$	6 s. 1 m.	0.57 0.55	0.47 0.53
Same	Platinum or gold in sodium sulphate $\frac{1}{10}$	15 s. 3 m.	0.12 0.10	0.08 0.08
Same	Platinum or gold in zinc sulphate $\frac{1}{10}$	10 s. 5 m.	0.26 0.23	0.09 0.01
Same	Platinum or gold in HCl $\frac{1}{10}$	15 s. 3 m.	0.45 0.41	0.24 0.28
Same	Platinum or gold in sodium chloride $\frac{1}{10}$	6 s. 3 m.	0.23 0.20	0.09 0.14
Same	Platinum or gold in zinc chloride $\frac{1}{10}$	10 s. 3 m.	0.29 0.24	0.18 0.17
Same	Platinum or gold in acetic acid $\frac{1}{10}$	12 s. 3 m.	0.32 0.31	0.28 0.30
Same	Platinum or gold in sodium acetate $\frac{1}{10}$	15 s. 3 m.	0.20 0.19	0.06 0.07
Same	Platinum or gold in zinc acetate $\frac{1}{10}$	10 s. 5 m.	0.22 0.21	0.09 0.12

* Raoult's signs reversed.

E. M. F.'S OF PLATINUM-PLATINUM AND PLATINUM-GOLD ELEMENTS.

I. *Platinum-platinnm.*—Raoult (1863) has found: 1. That two plates of platinum, depolarized and immersed *at the same time* and *completely* in a solution of sulphuric acid form a couple without E. M. F.

2. Two plates of platinum depolarized, immersed at the same time, the one *completely*, the other partially, in a solution of sulphuric acid, form a couple in which the partially immersed plate constitutes the positive electrode.

3. Two plates of platinum depolarized, immersed completely, but *successively*, in a solution of sulphuric acid, form a couple in which the plate first immersed is positive. In a solution of nitric acid, on the contrary, the plate last immersed is positive.

II. *Platinum-gold.*—A plate of gold and a plate of platinum immersed simultaneously in the same liquid which does not attack them form a couple the current of which varies in strength and intensity according to the nature of the liquid.

Exciting Liquid.	Pole +	Pole −	E. M. F. after an Immersion of	
			10 sec.	3 min.
			volts.	volts.
Concentrated sodium nitrate............	Platinum	Gold	0.226	0.216
Silver nitrate in 10 parts of water.......	Gold	Platinum	0.108	0.118
Sodium acetate in 10 parts of water	Platinum	Gold	0.129	0.118
Concentrated silver nitrate.............	Gold	Platinum	0.118	0.118

In certain liquids the E. M. F. of the platinum-gold couple varies with the time of immersion, so that the metal which in the beginning is negative, after a few minutes becomes positive.

Exciting Liquid.	− Electrode	+ Electrode	Time of Immersion.	E. M. F.
				volts.
Potash in 5 parts of water...........	Platinum	Gold	10 s.	0.032
Same	Gold	Platinum	10 m.	0.021
Nitric acid in 10 parts of water.........	Platinum	Gold	10 s.	0.010
Same	Gold	Platinum	10 m.	0.075
Sodium hyposulphite in 5 parts of water.	Gold	Platinum	6 s.	0.064
Same	Platinum	Gold	1 m.	0.064(?).

Polarization by Liquids or Solids.

In the following table by Raoult (1863) are given E. M. F.'s of certain couples formed of two metal plates of the same nature, A and B, immersed in the same liquid, but of which A acts as positive or negative electrode of a powerful cell, while the other, B, is perfectly independent.*

+
Copper A, serving as positive electrode in concentrated copper sulphate

−
Copper B, independent (non-polarized)   } 0.027 volt.

+
Copper A, serving as positive electrode in dilute copper sulphate

−
Copper B, independent (non-polarized)   } 0.054 "

+
Zinc A, serving as positive electrode in concentrated zinc nitrate

−
Zinc B, independent (non-polarized)   } 0.302 "

+
Platinum A, serving as positive electrode in concentrated nitric acid

−
Platinum B, independent (non-polarized)   } 0.108 "

+
Platinum A, serving as positive electrode in nitric acid + 5 vols. of water

−
Platinum B, independent (non-polarized)   } 0.324 "

−
Platinum A, covered with silver peroxide in concentrated silver nitrate

+
Platinum B, clean (non-polarized)   } 0.864 "

---

* Raoult's signs reversed.

$\overline{\text{Platinum}}$ A covered with manganese peroxide ⎫
$\overset{+}{\text{Platinum}}$ B, clean (in manganese sulphate) ⎭ 0.129 volt.

$\overline{\text{Platinum}}$ A, covered with lead peroxide ⎫
$\overset{+}{\text{Platinum}}$ B, clean (in lead nitrate) ⎭ .... 0.756 "

$\overline{\text{Platinum}}$ A, covered with silver peroxide ⎫
$\overset{+}{\text{Platinum}}$ B, clean (in silver nitrate) ⎭ .... 0.864 "

In a series of experiments made by H. Jahn (1886) the primary current was obtained from three Bunsen elements. The electrodes were strong sheets of platinum carefully washed. The values obtained with the different electrolytes used are given in the following table.

Temperature = 15°.

Electrolyte.*		Polarization.
Copper sulphate................	1.660	volts.
Cadmium "	2.364	"
Zinc "	2.715	"
Hydrogen " (sulphuric acid)..	2.388	"
Potassium "	3.118	"
Sodium "	3.136	"
Silver nitrate..................	1.220	"
Copper "	1.636	"
Lead "	2.143	"
Copper acetate..................	1.511	"
Lead "	2.043	"
Zinc "	2.624	"

* One molecule of salt per 200 H_2O. For copper acetate only a solution saturated at 0° was used.

In the following table the influence of heat is shown :

	Polarization at 0°.	Polarization at 34°.	Difference.
Copper sulphate	1.660 volts.	1.546 volts.	0.114 volt.
Zinc " ...	2.715 "	2.614 "	0.100 "
Silver nitrate.......	1.220 "	1.165 "	0.055 "
Lead "	2.143 "	2.061 "	0.082 "
Copper "	1.636 "	1.526 "	0.110 "
Lead acetate........	2.043 "	1.979 "	0.064 "
Zinc "	2.624 "	2.615 "	0.109 "

According to Beetz (1884), the depolarization of a platinum electrode polarized by oxygen is much more rapid than that of an electrode polarized by hydrogen ; for while, on one hand, the latter more profoundly penetrates the metal and is absorbed by the liquid, on the other hand, oxygen passes at the same time from the state of ozone to the inactive state.

F. Strenitz (1881) has studied polarization by hydrogen alone, before any apparent decomposition occurs, with platinum, gold, silver, and aluminium, using very dilute sulphuric acid. He concludes that the E. M. F. of polarization by hydrogen depends essentially on the nature of the electrodes. It is greater with gold, as Fromme (1881) had already found, and least with aluminium. Gold and silver lose in one minute the greater part of their polarization, and aluminium almost the whole. From a certain period onward, the polarization of palladium maintains a constant value, while with the other metals it always diminishes. Aluminium presents one abnormal peculiarity, which is that as soon as the cell is opened a reversal of polarization takes place, whatever may be its period of action. These different observers have studied polarization after one minute (or several) of rupture of the primary current.

Relation between the Polarization and the Nature of the Electrolyte. (Krieg, 1886.)

All the values in the following table have been measured after $\frac{1}{10000}$ to $\frac{1}{20000}$ of a second, open circuit. α represents

the diminution of current, or of E. M. F. referred to the unit of current during unit time, with electrodes of unit surface.

I.

Platinum Electrodes.

Electrolytes.	Value of the Constant α.
Solution of sodium chloride	0.42621
" " " bromide	0.19543
" " " iodide	0.04433
" " potassium chloride	0.39752
" " " bromide	0.17616
" " " iodide	0.09638
" " " sulphate	0.31845
" " sodium sulphate	0.31539
" " copper "	0.09230
" " iron "	0.08157
" " manganese "	0.18349
" " lead acetate	0.04971

II.

Potassium Chloride.

Electrodes.	Average Values of α.
Gold	0.00367
Silver	0.09201
Nickel	0.25579
Aluminium	1.30103
Platinum	0.39752

Potassium Bromide.

Gold	0.06579
Silver	0.05001
Nickel	0.17438
Aluminium	0.77815
Platinum	0.17616

Potassium Iodide.

Electrodes.	Average Values of α.
Gold	0.08200
Silver...............................	0.04671
Nickel...............................	0.16147
Aluminium	0.90309
Platinum............................	0.09638

III.

On arranging the different metals in the order of rapidity of polarization, the following series is obtained :

Potassium Chloride.

Aluminium, Platinum, Nickel, Silver, Gold.

Potassium Bromide.

Aluminium, Platinum, Nickel, Gold, Silver.

Potassium Iodide.

Aluminium, Nickel, Platinum, Gold, Silver.

The depolarization is therefore most rapid with aluminium, and slowest with gold and silver.

On open circuit, polarization diminishes slowly with gold and silver, and very rapidly with aluminium, with which a change in the direction of polarization takes place after $\frac{1}{500}$ to $\frac{3}{500}$ of a second with the chlorides of sodium and potassium.

Capacity for Polarization.—R. Blondlot (1881) has determined the following laws :

1. The initial capacity is independent of the direction of polarization.

2. The elementary capacity of an electrode for a given E. M. F. does not depend on the nature of the electrolyte.

Whence the following propositions : In order to change by instantaneous polarization the E. M. F. existing between an electrode and an electrolyte of a value e_1 to a value e_2, the

quantity of electricity required is always the same, whatever may be the chemical nature of the electrolyte. *Corollary:* The energy exerted is equally invariable.

3. The charge of the double electric layer existing at the surface of contact of an electrode and an electrolyte does not depend on the nature of the electrolyte, provided that the electric difference remains the same. *Corollary:* The potential energy of the double layer depends only on its E. M. F.

TABLE OF INITIAL CAPACITIES FOR THE SAME ELECTRODE. (R. BLONDLOT, 1881.)

	Platinum.
Acidulated water (with sulphuric acid)	Unity.
Solution of sodium sulphate	0.96
" " zinc "	1.00
" " copper "	1.00
" " sodium chloride	1.00
" " nickel "	1.10
" " copper nitrate	1.01
" " potassium iodide	1.00
Water acidulated with sulphuric acid + .0002 chromic acid	1.33
Water acidulated with sulphuric acid + .0002 potassium permanganate	1.28
Soda solution	1.50
Potash solution	1.50
Water acidulated with hydrochloric acid	0.75
Concentrated hydrochloric acid	1.19

Du Moncel (1873) has observed that a solution of pure mercuric sulphate produces, with a mercury cathode, a barely appreciable secondary current; but a few particles of sodium bicarbonate or zinc sulphate in this solution suffice to produce an energetic secondary current.

When mercury forms the anode, very energetic secondary currents are equally produced, which are most commonly due to the oxidation of the mercury and the reduction of the salts

resulting therefrom by the hydrogen condensed on the cathode. These currents are much less durable than those which are formed at the cathode, and the most important which have been recognized are those resulting from solutions of sulphate of sodium or iron, or ammonium chloride. Hughes (1880) has observed that when an iron rod has received its maximum of hydrogenation it becomes very slightly susceptible of yielding polarization effects even on short circuit, when a voltaic couple is formed with it. On comparing the zinc and hydrogenated iron couple with the Smee couple there has been found while the circuit has remained closed a higher E. M. F. in the proportion of 0.56 volt to 0.446 volt, and a polarization five times greater.

Polarization of Electrodes produced by Alternating Currents.—A polarized electrode may be likened to a charged condenser. If E represents difference of potential due to polarization, and Q the quantity of electricity necessary to produce this difference of potential E, we have

$$Q = CE.$$

Overbeck (1883) on using alternating currents for charging found that the polarization capacity of the majority of metals, and especially of the oxidizable ones, varied at the beginning of the experiment. Copper is notably oxidized by the effect of the current. The average polarization capacity per square millimetre approaches in salt water the following values:

Silver.....................	0.60 microfarad.
Gold.......................	0.30 "
Palladium	0.27 "
Platinum	0.18 "
Aluminium	0.05 "

Overbeck calculated from this the thickness necessary for an air-plate condenser of the same capacity per unit of surface, and found as follows:

Silver .... 147.10^{-10} mm. | Platinum.. 491.10^{-10} mm.
Gold......... 295.10^{-10} " | Aluminium 1768.10^{-10} "
Palladium .... 327.10^{-10} " |

Deformation of Polarized Electrodes (Gouy, 1883).—This phenomenon consists in a flexure which electrodes undergo in polarizing, when they are formed of thin metal plates having one face protected by a very light coating of insulating varnish.   From a gold ribbon rolled to a thickness of 0.015 mm. a strip 2 mm. broad was cut, terminating in a fine point.   This strip, varnished on one face, was so held that its end was left free for a distance of 0.06 m.   This extremity was placed vertically and entirely immersed in the solution contained in a cell having parallel sides.   The point was observed through a microscope.   The strip was connected to the positive terminal of a Daniell element ; the other electrode being of copper and connected to the negative terminal.

In these conditions the gold plate became polarized, although there was no persistent electrolysis and no gas-bubbles produced.   On the circuit being opened, the point became displaced and polarization diminished.   When the circuit was again closed, the point returned to its original position.   The direction of displacement showed that the strip curved from the non-varnished side, the absolute value of the displacement being 0.1 mm. and its apparent value about 0.02 mm.   The displacements appear more sudden when a small quantity of copper is deposited on the gold plate.   As soon as the copper is dissolved the electrode polarizes, a rapid deformation follows, and the apparatus works as before.

The deformations accompanying polarization have been observed in acidulated water and various solutions with gold and platinum for positive polarization, and with the same metals, as well as silver, copper, brass, lead, and tin, for negative polarization.   They vary in direction and magnitude, according to circumstances, within very extended limits.   Gold polarizes positively in manganese nitrate and gives enormous distortions, at least 200 times greater than those above indi-

cated. The metal during this experiment becomes coated with manganese binoxide.

Variation of Polarization Currents with Time.—A current traversing an electrolyte is interrupted, and after a very brief determinate time the polarization current is observed with a galvanometer. If i is the intensity of this current taken at a time t after the interruption of the first, the conditions appear to be $i = Ie^{-\alpha t}$; in reality the current diminishes less than this formula indicates. If α be determined for small values of t, this is found to decrease as the initial polarization is more energetic; but the E. M. F. e and the surface of the electrodes remaining the same, α varies inversely as the resistance. This value varies when the electrolyte changes, and appears one half less for hydrochloric acid than for sulphuric acid. (Bernstein, 1875.)

Change of Direction of Polarization produced by Alternating Currents.—The current from a Bunsen element is passed into a voltameter charged with distilled water and having as electrodes two large plates of platinum. At the end of ten seconds the current-direction is reversed, and it is allowed to pass for three or four seconds. If now the circuit be opened, the polarization current is at first directed as if the second current only had existed; then it weakens rapidly and changes direction. If the current had lasted more than three or four seconds, only the first polarization current would be observable; if it had had a shorter duration, the polarization produced by the first current only would be observed.

"Singular" Polarization of Electrodes.—The term "singular polarization" was applied by Sokoloff (1881) to the condition when the depolarizing current is considerably stronger (six or eight times) than the primary current. "Singular" polarization appears with acidulated water only in voltameters closed and free from air—never in open voltameters. The depolarization current is the more intense at the beginning, as the surface of the electrodes is small and the resistance low; but the duration of the phenomenon is inversely as its intensity. The "singular" phenomenon appears more or less rapidly after

the closing of the primary circuit; generally after from 17 to 24 hours it has considerable development.

The following experiment is illustrative: A tube containing two platinum electrodes is filled with water acidulated with sulphuric acid, exhausted of air, and hermetically sealed. This is connected with a Daniell element. If the latter be allowed to act for several hours, a galvanometer in circuit being observed, and if the polarized electrodes be discharged without alteration of the resistances, there is obtained during the first moments a current four or five times stronger than the polarizing current. In this experiment the galvanometer resistance used was 3542 ohms.

There exists, however, a certain limit of the polarizing E. M. F. below which "singular" polarization never manifests itself. In the majority of cases this was found to be 0.496 volt.

A strong "singular" polarization (though weaker than that noted with closed voltameters) was found with open voltameters using solutions of lead nitrate, sulphates of manganese, cobalt, and nickel, and bismuth nitrate. The deposits of peroxide, except in the case of the manganese salts, are not produced except in open voltameters. A certain minimum E. M. F. is always necessary in order that singular depolarization may appear: 0.16 volt for solutions of manganese sulphate and 0.594 volt for those of lead nitrate.

No "singular" depolarization has been observed either with silver nitrate or sulphate, although the formation of peroxide was visible even before electrolytic decomposition took place. "Singular" depolarization is always manifested with the sulphates of zinc, cadmium, and aluminium on using the E. M. F. of one Daniell element, whether the voltameter be exhausted of air and closed or quite open; but in the first case it is more energetic and lasts longer. The nitrates and sulphates of the alkalies and alkaline earths all manifest "singular" depolarization; but while with the open voltameter the galvanometer impulse is of short duration, with a closed voltameter the phenomenon continues for from thirty to fifty minutes after the beginning of the discharge.

CHAPTER XX.

ACCUMULATORS OR "STORAGE" CELLS.

A SECONDARY voltaic cell or voltaic accumulator is one in which the means for the development of chemical action is normally present, but is not active until so rendered by a chemical alteration produced by an electric current from another source.

Gas cells (see p. 320) have already been considered. The term "storage" cell is a misnomer—although it now has the sanction of long custom—for, as is obviously the case, there is no "storage" of electricity nor of anything else in the apparatus.

The idea of using oxidizable metals as electrodes in secondary cells to produce useful currents is generally attributed to Sinsteden (1854). Planté himself says:

"In a memoir on the effects of a magneto-electric apparatus, Sinsteden, having caused the current of the apparatus incidentally to act on voltameters having plates of lead, silver, and nickel, obtained with these metals secondary currents sufficiently intense to bring metallic wires to incandescence."

The development of secondary currents dates, however, from the beginning of the century, and is abundantly discussed in the recorded investigations of Gautherot, Ritter, Erman, Volta, Davy, Becquerel, Marianini, and others. The " Manuel du Galvanisme " of Joseph Izarn (Paris, 1804) contains the most complete account of these early researches.

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" Positive " and " Negative " Electrodes in Accumulators.—The confusion in the use of the words " positive " and " negative," as applied to the parts of a primary cell, has become even worse confounded in the application of these terms to the accumulator. Of this fact any one may convince himself by placing in contrast a selection of the existing textbooks made almost at random. If A and B represent the two electrodes in the cell, and a current from an outside source be conducted to A so that it pass through the electrolyte to B, and so back to the source, then A is the positive electrode and B is the negative electrode. A is at the anode and B is at the cathode ; and this is the condition of affairs when the cell is being charged. When, however, the charging source is removed and the cell, thus rendered active, delivers its own current, then the current direction is reversed, and it proceeds in the electrolyte from B to A ; therefore B is then the positive electrode and A is the negative electrode. Just as in the case of the primary cell, where the main confusion arises from the fact that the writers fail to state whether they regard one electrode as positive to the other or the reverse with reference to the direction of current outside of the cell or to the direction of current through the electrolyte inside of the cell, so, in the case of the accumulators, a new difficulty presents itself when the terms " positive " and " negative " are used without any statement as to whether they refer to the condition of the cell when it is being charged or when it is yielding its own current. As a rule, the electrode B in the above illustration is always called the " negative " electrode ; although, as a matter of fact, when the cell is fulfilling its function and delivering its current, the plate B is not the negative electrode, but the positive electrode. Sir David Salomons, in his work on "Accumulators," says: " It has become a practice among makers of secondary cells to call the true positive, negative, plates, and *vice versa ;* therefore, not to cause confusion, the manufacturers' designations will be adhered to throughout." It is hardly necessary to base a choice of terms upon any such convention as this if it be generally understood that in all cases the employment of the words refers

to the relation of the electrodes during the charging operation. In the following pages the words " positive " and " negative " are used in this sense.

Types of Accumulators.

Accumulators are here considered under the following divisions :

I. Accumulators of the Planté type having lead electrodes.
> (*a*) The electrodes are lead plates, wires, or granulated lead.
> (*b*) The electrodes are of spongy, porous, or crystallized lead.
> (*c*) The electrodes are of amalgamated lead.

II. Accumulators having supports containing or covered with non-electrolytic lead oxide.

III. Bimetallic accumulators ; the positive electrode being usually of lead, and the negative electrode of zinc, copper, etc.

IV. Other forms of accumulators.

V. General practical data, tables, etc.

I. Accumulators of the Planté Type.

(*a*) The electrodes are lead plates, wires, or granulated lead.

Planté Accumulator (1860).—This consists of two long and broad sheets of lead rolled in a spiral and separated from one another by coarse canvas, the whole being immersed in a jar containing water with 10 per cent sulphuric acid. In 1872 Planté changed the manner of separating the lead plates, substituting for the cloth, strips of rubber about 1 cm. in breadth and .5 cm. in thickness (Fig. 135). Fig. 136 shows a complete Planté accumulator of this type connected in circuit with two Bunsen charging elements.

Planté Accumulator with Parallel Plates (1868).—This consists of several plates closely approximating, but separated at
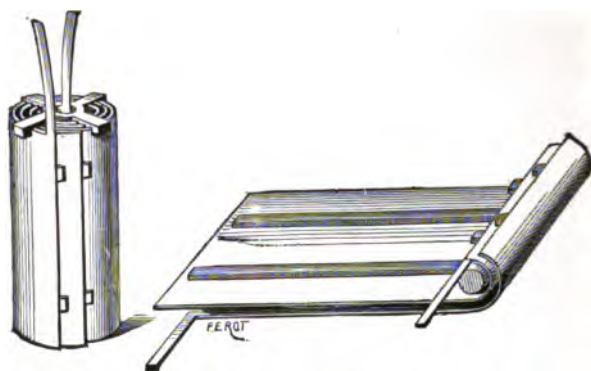
FIG. 135.—PLANTÉ ACCUMULATOR.
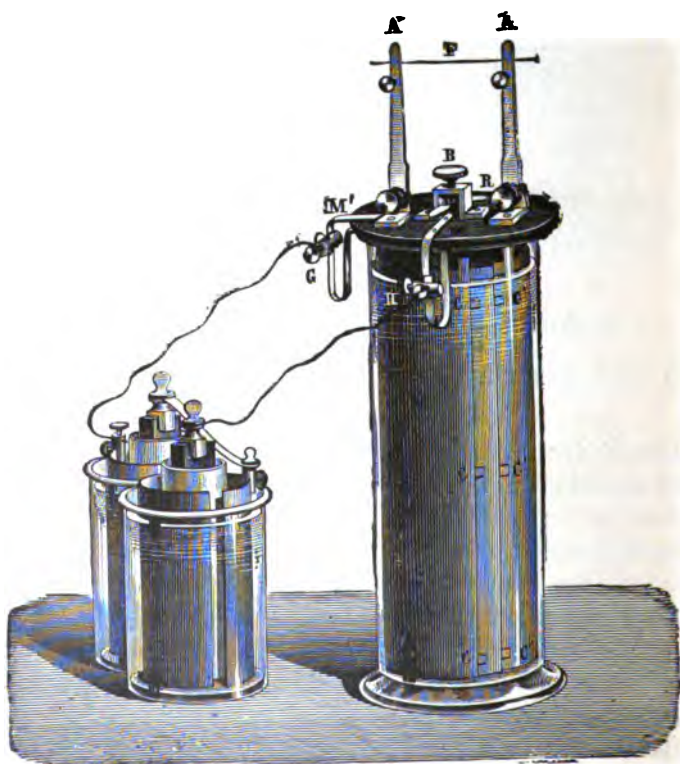
FIG. 136.—PLANTÉ ACCUMULATOR.

their middle portions by insulating rods. They are placed vertically and in two series, projections on alternate plates being electrically united. The whole is contained in a gutta-percha vessel rectangular in form and having interior grooves in which the plates are received and held parallel. The liquid is a 10 per cent sulphuric acid solution. In order to " form " his accumulator Planté proceeds as follows: The current from two Bunsen elements is caused to pass through the electrodes of the accumulator six or eight times in alternately opposite directions during the first day. The time during which the cell is submitted to the action of the primary current before reversal is gradually increased, and care is taken to discharge the accumulator before each change of current direction. The following table prepared by Tamine shows the duration and direction of the first twenty charges.

| No. of Charge. | Duration of Charge. | |
	Direct Current.	Reverse Current.
1	$\frac{1}{4}$ hour	—
2	—	$\frac{1}{4}$ hour
3	$\frac{1}{2}$ hour	—
4	—	$\frac{1}{2}$ hour
5	$\frac{3}{4}$ hour	—
6	—	$\frac{3}{4}$ hour
7	1 hour	—
8	—	1 hour
9	$1\frac{1}{4}$ hours	—
10	—	$1\frac{1}{4}$ hours
11	$1\frac{1}{2}$ hours	—
12	—	$1\frac{1}{2}$ hours
13	$1\frac{3}{4}$ hours	—
14	—	$1\frac{3}{4}$ hours
15	2 hours	—
16	—	2 hours
17	$2\frac{1}{4}$ hours	—
18	—	$2\frac{1}{4}$ hours
19	$2\frac{1}{2}$ hours	—
20	—	$2\frac{1}{2}$ hours

After being once "formed" the accumulator is always charged in the same direction. The primary current no longer does useful work toward the production of the secondary current when its energy is expended in disengaging gas-bubbles at the electrodes of the accumulator.

Rapid Formation of Lead Plate Accumulators (Planté).—This process consists in submitting the secondary couples simply to a deep scouring by nitric acid diluted with one half its volume of water, leaving them immersed in the liquid for from 24 to 28 hours. The vessels are then emptied and, with the plates, thoroughly washed with water, then refilled with water containing 10 per cent sulphuric acid and again subjected to the action of the primary current. The nitric acid partially attacks the lead plates, and thus renders them more permeable to the gases coming from the decomposition of the water. Secondary couples thus treated may yield in eight days, and after three or four reversals of the primary current, currents of long duration which without the nitric acid treatment could not be obtained until after several months' forming. When a new or an already formed accumulator has rested for a long time, gases will be disengaged at the surface of the plates, and the maximum degree of charge will not be obtained.

Lead peroxide has a great tendency to become spontaneously reduced in acidulated water as fast as it is formed. This reduction is the easier as the coating is the more slowly deposited, so that there comes an instant when the action of the primary current, tending to renew or maintain the coating on the surface of the plate, is balanced by the tendency of the peroxide to reduce itself as above stated. Lead covered with lead peroxide behaves in water acidulated with sulphuric acid in exactly the reverse way as does zinc in the same liquid. It tends to decompose water while seizing the hydrogen, and to become the negative electrode of the cell, if associated with non-oxidized lead, while pure zinc tends to decompose water while seizing oxygen and becomes the positive electrode of the couple which it forms with another metal.

Yield.—Planté has found that the yield of his accumulators

is 88 to 89 per cent. The causes of loss of work corresponding to 11 or 12 per cent are the following :

1. The spontaneous reduction in acidulated water of a small quantity of the lead peroxide as fast as it is deposited on the platinum plate.

2. The incomplete formation of the accumulator.

3. Polarization or the development of an inverse E. M. F. in the accumulator itself during operation.

Coulombs yielded by a Planté Accumulator according to the Period of Forming.

Time.	Coulombs per Kilo of Lead.
150 hours.............................	5,000
500 "	10,000 to 12,000
Accumulator very old and well formed......	36,000

Relation of the Surfaces of the Electrodes.—Pezzer has determined by repeated experiments that the accumulator in which the surface area of the negative lead electrode is double that of the positive electrode is more efficient than one in which these conditions are reversed.

Constants of the Planté Accumulator according to E. Reynier.

Surface of the positive electrode..........	60 sq. dcm.
" " " negative electrodes.........	120 sq. dcm.
Weight of the positive electrode..........	2.100 kg.
" " " negative electrodes.........	4.200 kg.
E. M. F. during discharge................	1.85 volts.
Average resistance......................	0.04 ohm.
Normal intensity of discharge current......	7 to 8 amperes.
Intensity of charging current.............	1 to 5 "
Capacity of ac- ｛ After 300 hours' formation	100,000 coulombs.
cumulation ｛ " 500 " "	150,000 "

Tamine concludes that the normal yield of discharge current is exaggerated for elements of the Planté type, and that

it need seldom exceed 0.75 ampere per kilogram of electrode. This would amount for 6300 kg. to about 4.5 amperes.

The Separation of Planté Electrodes.—M. Planté regarded this as of the greatest importance, and as the result of his extended experience finally adopted the method illustrated in Fig. 137. The lead plates are kept apart by a series of " dou-
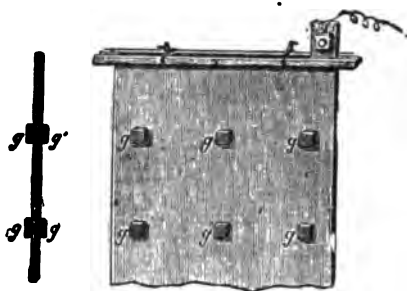
FIG. 137.—PLANTÉ ELECTRODE.

ble buttons " of gutta percha, as gg', shown in the accompanying illustration : these are placed about 4 inches apart, but may be placed closer so as to avoid any possible contact of the plates. In order to attach the buttons firmly the alternate plates are perforated with holes about ¼ inches in diameter, and a cube or small cylinder of gutta percha is pressed against each.

The gutta percha is first softened by the heat of a candle or alcohol lamp, and then a similar piece is pressed in from the other side of the plate. The two pieces unite at the joint and form the double button gg', which adheres firmly to the plates and assures their insulation. As stated before, it suffices to treat only the alternate plates in this manner.

The plates are suspended by means of strips of wood attached to them by lead wires, the ends of the strips resting against the sides of the containing vessel. These wires, however, must be placed on the adjacent plates so as not to touch one another.

The projecting piece of each plate is varnished or dipped in a resinous mastic and provided with a nut of copper or type-metal, by means of which any number of plates can be connected by bars.   The independence of each plate is thus assured, and any one of them can be lifted out without interfering with the position of the others.

Encausse and Canésie Accumulator.—The electrodes are lead plates rolled in helical form.

Fox Accumulator.—Superposed sheets of lead with interposed layers of sand, asbestos paper, etc.

Kabath Accumulator.—The commercial form consists of a thin perforated lead chamber packed with a large number of lead strips, each alternate one of which is corrugated or fluted. A chamber 8.5 cm. wide contains about 180 of these strips, and is covered on the faces with a perforated lead.   Each composite plate weighs about 1 kilogram.   The electrolyte is distilled water to which $\frac{1}{10}$ sulphuric acid is added.   The following table shows the principal data of the forming process of a commercial battery containing 12 plates, the weight of the electrodes being 21 kilos; electrolyte, etc., 6 kilos; box, 3 kilos—total, 30 kilos.

Number of Hours' Formation.	Capacity per Kilo of Lead.		Weight of Lead per Horse-power in Kilograms.	Energy stored in Accumulator.	
	Kilogram-metres.	Coulombs.		Kilogram-metres.	Horse-power Hour.
75	750	5,000	360	15,750	0.058
150	1,000	6,250	270	21,000	0.078
500	2,000	12,000	135	42,000	0.155
1000	3,250	19,000	83	88,250	0.253
1600	4,750	28,000	57	99,750	0.369
2000	5,750	34,000	47	120,750	0.447
2600	7,250	43,000	37	152,250	0.564
3000	8,250	49,000	32.8	172,250	0.642
4000	10,750	64,000	25	225,750	0.836

Parod Accumulator.—The plates consist of copper cores hermetically enclosed in a lead covering.

Jarriant Accumulator.—Lead granules form both the positive and the negative electrodes. They are held in porous envelopes.

Pezzer and Carpentier Accumulator (1881).—The electrodes consist of a number of undulating bands of lead connected by autogenous soldering. One electrode is immersed in a vessel of acidulated water, and the other in an outer vessel filled with the same.

De Meritens Accumulator.—Small plates of lead 15 cm. square by a few tenths of a millimeter thick, piled one on the other so that between each there is a narrow interval which allows of circulation of dilute sulphuric acid. The laminæ are folded upon one another and then soldered to a strong lead framework. The electrolyte is dilute sulphuric acid.

Tamine Accumulator (1866).—The positive plate is of plates joined together, and the negative is a thin sheet of lead about 1 mm. in thickness. E. M. F. = 2.3 volts. The liquid consists of

Saturated solution zinc sulphate........ 1000 parts.
Sulphuric acid at 10°................... 500 "
Ammonium sulphate................. ..... 50 "
Mercury   "   .... 50 "

Solution is first made of the sulphate of ammonium and sulphate of mercury. This is poured into the acid, and the zinc sulphate added. The element is formed in an ordinary acidulated bath and then slowly discharged in the above liquid.

Arnould and Tamine Accumulator, No. 1.—Around a rod of glass is wound a long lead wire so that the turns touch. Outside of this is a covering of parchment-paper held in place by woollen thread. Another superposed lead spiral is covered as before with parchment-paper. There are four or five of these spirals, the ends of which form terminals of the cell. The whole is placed in dilute sulphuric acid. Parchment-paper, say the inventors, becomes rapidly destroyed, forming a pulp and allowing the electrodes to come into contact. They have tried a great variety of substances, but find nothing that

will stand for six months. They consider very thin disks of porous earth better than any other arrangement.

Montaud Accumulator (1885).—Rectangular lead plates arranged as shown in Fig. 138. Details are represented in
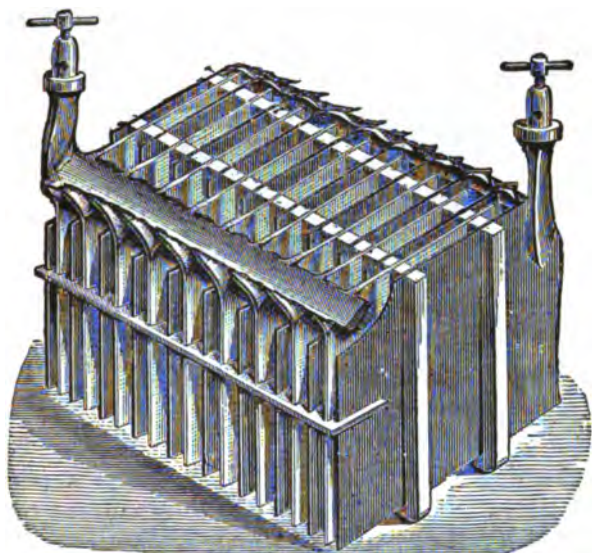
FIG. 138.—MONTAUD ACCUMULATOR.

Figs. 139, 140, 141. The plates are covered with lead electrolytically produced from a solution of potassium plumbate.
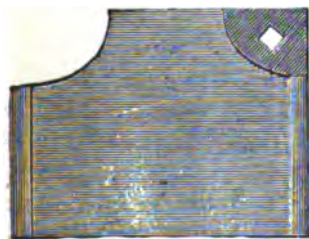
FIG. 139.   MONTAUD ELECTRODE AND FASTENING ROD.   FIG. 140.

These electrodes therefore differ from those of Planté, in being "formed" in a solution of potassium plumbate instead of in dilute sulphuric acid.

Lead thus treated is in a porous condition. The shape of the plates is shown in Fig. 139. Each is pierced with a hole to receive the rod of lead or white metal (Fig. 140) which connects them together and forms a terminal. The plates are separated by wooden combs, one of which is shown in Fig. 141. The best results with this cell have been obtained
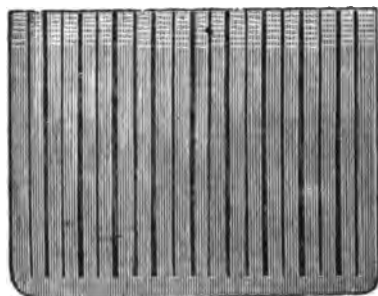
FIG. 141.—MONTAUD COMB.

with a charging current density of 10 amperes per square metre of active surface and a discharging current of 20 amperes. With a cell containing 2 square metres of lead surface D'Arsonval has obtained the following : Useful capacity, 40 ampere-hours; total capacity, 62 ampere-hours; charge, 10 amperes per square metre ; discharge, 20 amperes per square metre ; useful weight of lead, 10 kilograms.

Arnould and Tamine Accumulator, No. 2.—The plates consist of a series of parallel lead wires of the same length and having as many points as possible. The cell terminals are united by autogenous soldering.

E. Reynier and Simmen Accumulator (1885).—The original Simmens plate consisted of lead filaments pressed together. These filaments were obtained by pouring melted lead into a previously heated vessel, the bottom of which is perforated and provided at the perforations with short tubes (ajutages) of suitable dimensions and form. The metal runs in jets through these tubes and is quickly cooled in a basin of water, to the bottom of which it falls in solid condition. This material is termed

lead wool, and it is of remarkably fine texture. When pressed into blocks and enclosed in a perforated lead chamber it offers a very large active surface.

Simmen's agglomerated plates did not prove successful, owing to the rapid destruction of the lead-containing chambers. He afterwards, in conjunction with M. Emile Reynier, materially improved them by constructing them of masses of lead wire compressed in a strong metal frame. The average diameter of the wire of the positive electrode was 0.5 mm. and of the negative electrode 0.2 mm. A plate 140 mm. wide, 245 mm. high, and 4 mm. thick weighs 700 grams, has a surface of 5.4 square decimetres, and a current capacity of 17 ampere-hours, or per kilogram of plate a capacity of 7.3 ampere-hours.

E. Reynier Accumulator.—The plates are bent and encased
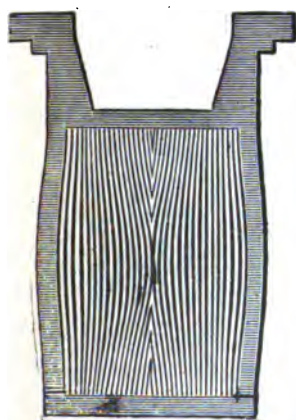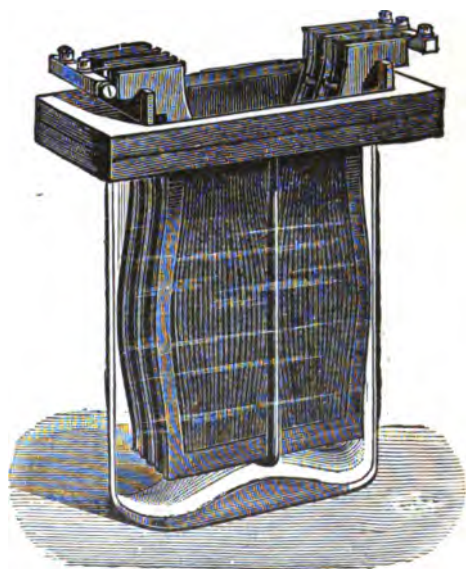
FIG. 142.   REYNIER ACCUMULATOR.   FIG. 143.

in a frame having projections which serve as supports and conductors, Fig. 142. There are several forms of this apparatus. Fig. 143 represents a battery of five plates.

In the so-called "elastic" accumulator of **Reynier** the plates consist of very fine lead wires made into a net and compressed into shape. They are separated by thin porous sheets of silica. The plates are placed between rigid end-pieces drawn together by india-rubber springs which allow of their contraction and expansion. The following data are given of a 15-cell battery: Total E. M. F., 32 volts; E. M. F. at terminals, 28 volts; rate of discharge, 3 to 6 amperes; average available energy, 150 watts; capacity, 30 ampere-hours; available work, 740 watt-hours; total weight of battery, 110 lbs.

Bernados Accumulator (1887).—The electrodes consist of lead frames in which are soldered numerous strips of the same metal alternately straight and corrugated. Fig. 144 represents
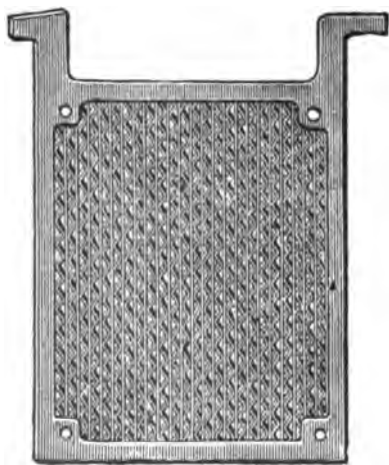
FIG. 144.   BERNADOS ACCUMULATOR.   FIG. 145.

a plate of this kind, and Fig. 145 a straight and a corrugated lead strip.

Elwell and Parker Cylindrical Accumulator.—The electrodes are perforated sheets of lead rolled spirally into tubes and placed alternately positive and negative in an earthenware vessel. A space of about $\frac{1}{2}$ inch is left between the tubes, which are held together by screw-clamps.

Epstein's Method of Forming consists in placing the plain lead plates in a one per cent solution of nitric acid and water. The solution is then boiled until the lead plates become of a dull gray color, when they are dried in air. In forming the positive electrodes the operation is continued until the color changes to a dark brown; and in forming the negative electrodes the color is allowed still further to change to a bluish gray. The plate is made with deep grooves on both sides. The normal maximum rate of discharge is given as 30 amperes per positive plate, and for short periods this rate may be safely doubled. The capacity at the above rate is from 120 to 150 ampere-hours per positive plate; at half this rate, from 140 to 170 ampere-hours. The electrolyte is a 10 per cent solution of sulphuric acid and water.

Cheswright Accumulator.—The electrodes are of refined sheet lead corrugated into a series of raised dovetail-shaped rims, hollow, and divided into vertical chambers by thin lead partitions. During the formation of the peroxide plate the active material forces itself into and so becomes locked in the dovetail grooves, which are arranged closer together than on the spongy lead plate. The current capacity is stated to be from 7 to 9 ampere-hours .per kilogram of plate, depending upon the dimensions of the cell. The working current efficiency is given as from 80 to 90 per cent.

(*b*) THE ELECTRODES ARE OF SPONGY, POROUS, OR CRYSTAL-LIZED LEAD.

Sellon and Volckmar Accumulator.—The electrodes are lead plates having holes of different shapes. The plates are 4 mm. thick, and the holes are separated about 2 mm. from one another and filled with spongy lead.

Changy Accumulator.—The electrodes are granular masses of lead produced by melting the metal and then projecting it upon a cooled surface. The containing vessel is divided by a porous partition into two compartments, each containing a

lead plate. The compartments are filled with the granulated lead.

Watts Accumulator.—The plates are made of a sort of compressed lead powder; the latter being produced by subjecting a stream of melted lead to a blast of steam or superheated air. The finely divided metal is condensed in a cool receptacle.

Kabath Accumulator, No. 2.—The electrodes consist of envelopes of perforated lead filled with spongy lead obtained by precipitating an 8 per cent solution of lead acetate by a zinc plate, and washing the metallic deposit.

Pfeifer Accumulator (1883).—Plates of lead covered with a coating of spongy lead obtained by electro-decomposition of lead acetate.

Fitzgerald, Crompton, Biggs and Beaumont Accumulator (1882).—Electrodes of very porous lead obtained by electrolytic action on alloys of sodium, zinc, cadmium, iron, antimony, or copper formed of one or more of these metals and lead. The object of the electrolysis is to eliminate the added metals, thus leaving the lead in a spongy state.

Monnier Accumulator (1884).—Plates of spongy lead obtained by treating an alloy of zinc and lead with soda and sulphuric acid. An accumulator containing 19 kg. of plates and 4 kg. of acidulated water weighs in all 29 kg. It yields 23 amperes, with an E. M. F. of 1.86 volts, and furnishes 520,000 coulombs (144 ampere-hours), representing about ⅓ horse-power-hour. (E. Reynier.)

Garasseno Accumulator (1889).—The plates are made of ribbed castings, and each positive plate is permanently connected to the negative of the next cell by having one lug in common perforated (Fig. 146). The ribs are on both sides of the plate, with a thin dividing web. The recesses are filled with precipitated metallic lead in a perfectly porous state. A cell containing fifteen such plates weighs, complete, 25 kilograms, and is said to give an average capacity of 150 ampere-hours, with a discharge rate of 30 amperes.

Schulze Accumulator.—In order to produce electrodes of spongy lead, lead plates are covered with a paste of sulphur

and heated so that a coating of lead sulphide is thus formed. By the action of the current the sulphur is separated and the plates become spongy.
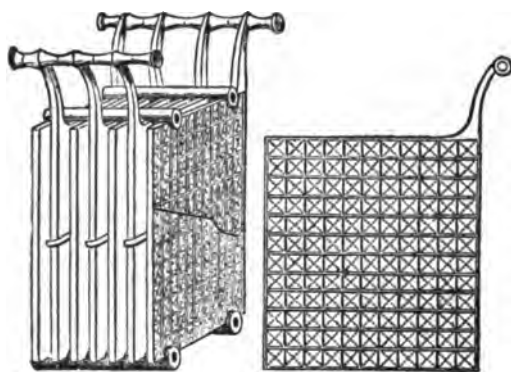
FIG. 146.—GARASSENO ACCUMULATOR.

F. Leclerc and C. Payen Accumulator (1885).—The electrodes are formed of porous crystallized lead obtained as follows : Chloride of lead to which from 5 to 10 per cent of zinc chloride is added is melted and run into moulds. After cooling, each plate is placed between two zinc plates and plunged in a solution of ammonium chloride. When all the lead chloride has been reduced by the zinc, the plates are withdrawn, washed, and formed in the usual way.

Dujardin Accumulator.—The electrodes are made up of corrugated lead plates, the corrugations running obliquely across the surface in opposite directions on adjacent plates. They are rendered active in a bath of water 10 kilograms, sulphuric acid 2 kilograms, and 1 kilogram of alkaline nitrate (of soda, ammonia, potash, etc.). By the passage of a current lead nitrate is formed, which, by the acid present, is continuously converted, first into lead sulphate and then into lead peroxide. The positive plates become covered with an adherent layer of crystalline peroxide.

Dujardin-Drake and Gorham Accumulator (known in England as the D. P. cell).—Electrodes consist of narrow strips of lead with points or projections on their faces built up one above the other like the leaves in a book. The ends of the strips are lead-burned together. The capacity of a cell weighing 65 lbs. is given as 140 ampere-hours ; of one weighing 240 lbs., 725 ampere-hours. Formation is effected in the manner above described.

Crompton-Howell Accumulator.—The electrodes are of crystalline lead, on which the active material electrically deposited forms an adherent coating. No reversals occur in forming, the positive electrode being directly converted into lead peroxide and the negative electrode being reduced to the chemically spongy lead condition. The plates are held in position by celluloid combs. The actual energy efficiency is claimed to be about 86½ per cent.

Woodward Accumulator.—Molten lead and sodium chloride are mixed to form a plastic mass, then compressed into moulds, and finally the salt is dissolved out.

The general method followed by Woodward of incorporating with lead in a pasty state soluble matters which can afterwards be washed out, leaving the lead porous, has been followed by many other inventors. A still simpler plan, followed by W. E. Case and others, consists in melting the lead and then shaking the liquid mass in a receptacle until it becomes granular and somewhat pasty, after which it is compressed in moulds to form spongy plates.

Chemical Actions produced in Accumulators having Lead Electrodes.—*Planté's Theory.*—Under the action of the primary current the water is decomposed ; the oxygen peroxidizes the positive electrode and the hydrogen goes to the negative electrode, which is always more or less oxidized by the exposure to the air.

Faure's Theory.—Transportation of a certain quantity of oxygen from one electrode to the other in electro-chemical proportions, and transformation of Pb into Pb_2O, and of PbO_2 into Pb_2O_2.

Theory of Gladstone and Tribe.—During charge,

$$(\text{Electrode} +) \, SO_4Pb + O = PbO_2 + SO_3;$$
$$(\text{Electrode} -) \, SO_4Pb + H_2 = Pb + SO_4H_2.$$

During discharge,

$$\overset{-}{Pb} + 2SO_3 + Aq + \overset{+}{PbO_2} = \overset{-}{SO_4Pb} + Aq + \overset{+}{SO_4Pb}.$$
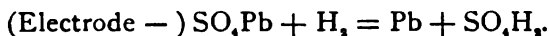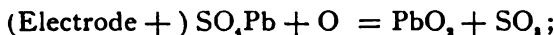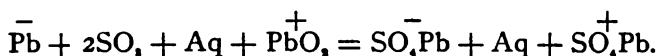
* During the charge there is reduction of the lead sulphate at the negative electrode and oxidation of the lead sulphate at the positive electrode, the products of which are lead peroxide and sulphuric anhydride, which last, on contact with water, is transformed into ordinary sulphuric acid. During discharge lead sulphate is produced on both electrodes.

Frankland's Theory.—During discharge the chemical effects are as follows :

1. Electrolysis of hexabasic sulphuric acid, as during the charge.

2. Transformation of sulphuric anhydride into hexabasic sulphuric acid.

3. The chemical action of the deposit on the positive plate is

$$PbO_2 + H_2 = PbO + H_2O.$$
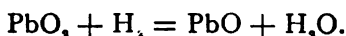
The lead oxide thus formed is immediately converted into lead sulphate,

$$PbO + SO_4H_6 = SO_4Pb + 3H_2O.$$
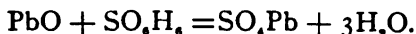
4. The chemical action on the deposit on the negative plate is

$$Pb + O + SO_4H_6 = SO_4Pb + 3H_2O.$$
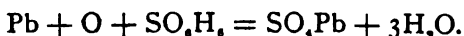
Thus during discharge, as during charge, the initial action is due to the electrolysis of hexabasic sulphuric acid. The oxygen eliminated on the positive plate converts the reduced metal in this plate into lead oxide, while the hydrogen transforms in the same oxide the lead peroxide of the other plate. In both cases this lead oxide is then converted into lead sulphate by the free sulphuric acid, both plates being thus brought back to the normal conditions existing before the beginning of the charge.

Tamine's Theory.—During the charge the sole effect of the primary current is to decompose the water H_2O, producing on the positive electrode a layer of lead peroxide PbO_2, and to reduce to the state of Pb on the negative electrode the coating of oxide there formed by the previous charge.

During the discharge the lead peroxide, by reason of its • great affinity for H, decomposes solely the water, and is brought to a lower state of oxidation, PbO, while the negative electrode becomes in turn coated with plumbic oxide, PbO. Such are the principal actions produced in a lead accumulator. But independently of these are produced secondary actions which result, not from electrolysis itself, but from the combination of the lead oxide formed on the two electrodes with the acid of the liquid. In brief, Tamine agrees with the opinions of Planté, and considers further the secondary action which follows the first. This secondary action may be formulated thus:

$$PbO + SO_4H_2 = SO_4Pb + H_2O.$$
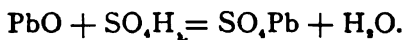
This is substantially Frankland's conclusion, with the difference that Tamine does not recur to the existence of a hexabasic sulphuric acid.

Thermo-chemistry of Accumulators. (Tommasi.)

The heat of formation of lead peroxide being known [(Pb + O = 12.14 cal. and Pb + O_2 = 63.14 cal. (Tscheltzow)],

the chemical reactions which occur in the two plates of lead accumulators may be examined.

According to Tscheltzow (1884), the four possible hypotheses are the following :

(*a*) PbO_2 may be reduced by the hydrogen of the negative electrode. The reaction gives

$$+ H_2O - \tfrac{1}{2}(PbO.O) - \tfrac{1}{2}(Pb.O) = 37.20 \text{ cal.}$$
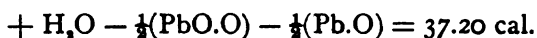
(*b*) PbO_2 may be transformed into SO_4Pb. The heat disengagement is then equal to .

$$+ (H_2O) + (PbO,H_2SO_4Aq) - (PbO.O) = 81.5 \text{ cal.}$$

(*c*) The negative lead may be transformed into sulphate, and PbO_2 into Pb.
The reaction gives

$$- (H_2O) + (PbO) + (PbO,H_2SO_4Aq)$$
$$- \tfrac{1}{2}(PbO,O) - \tfrac{1}{2}(Pb,O) + (H_2O) = 44.30 \text{ cal.}$$
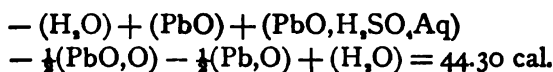
(*d*) There may be sulphating of both electrodes. The heat disengagement is equal to

$$- (H_2O) + (PbO) + (PbO.H_2SO_4Aq) - (PbO,O)$$
$$+ (H_2,O) + (PbO,H_2SO_4Aq) = 88.60 \text{ cal.}$$
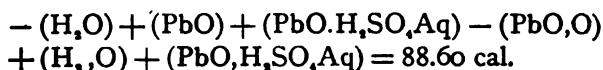
According to the formulas of W. Thomson and D. Tommasi, the reactions should give :

	W. Thomson.	D. Tommasi.
Reaction (*a*)	0.81 volt.	0.80 volt.
" (*b*)	1.77 "	1.76 "
" (*c*)	0.96 "	0.95 "
" (*d*)	1.93 "	1.91 "

Direct measurement gives for the E. M. F. of the lead accumulator from 1.9 to 2 volts. Thus, according to Tscheltzow, it may be regarded as well established that in the Planté couple the fundamental reaction consists in the sulphating of the two electrodes.

(*c*) THE ELECTRODES ARE OF AMALGAMATED LEAD.

Sutton Accumulator.—Amalgamated lead electrodes in dilute sulphuric acid. According to Sutton, the amalgamation of the plates causes them, when used as anodes, to be much more rapidly and uniformly peroxidized, and prevents local action.

Nezeraux Accumulator (1885).—Two cast-lead plates having channels on both faces, in which channels is held a mass of spongy lead amalgam the thickness of which beyond the containing channels is limited by a frame projecting around the plates. In order to obtain the lead amalgam the lead is melted in an iron vessel, and half its weight of mercury is added. After cooling, the amalgam is broken up with the hammer and sifted. The powder thus obtained is applied dry to the plates and compressed thereon. It forms a solid coating if wet with acidulated water and then exposed to the air for some days. The plates are finally disposed in a 10 per cent sulphuric acid solution, and submitted to the action of a current of from 1 to 2 amperes per kilogram. " The industrial storage capacity of this accumulator," says Nezeraux, " with plates containing 70 per cent of spongy lead and a withholding (*détente*) of only $\frac{1}{16}$ of the E. M. F., may attain 18,000 to 20,000 kilogrammetres per kilogram of plate."

Kalischer Accumulator (1886).—Positive, lead ; negative, amalgamated lead. The accumulator is charged with acidulated water containing a little mercuric chloride. The latter hinders the deposition of crystalline lead on the cathode.

CHAPTER XXI.

ACCUMULATORS. *(Continued.)*

II. Accumulators having Supports containing or covered with Non-electrolytic Lead Oxide.

Faure Accumulator (1881).—Lead plates to the surface of which is applied a coating of minium in the form of a compressed paste. The plates are covered with felt and immersed in acidulated water. E. M. F. = 2.057 to 2.165 volts. The committee presided over by Tresca at the Electrical Exposi-

FIG. 147.   FIG. 148.
FAURE-SELLON-VOLCKMAR ACCUMULATOR PLATES.

tion of 1881 obtained the following data concerning this accumulator. Yield in quantity (difference between the quantity of electricity in coulombs introduced into the accumulator and that which emerged therefrom) = 90 per cent. Yield in elec-

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tric work (stored energy) = 60 per cent. Yield in mechanical
work (total work) = 40 per cent. D'Arsonval has obtained as
corresponding data 84.34 per cent, 62.44 per cent, and 46.50
per cent.

Faure-Sellon-Volckmar Accumulator.—The plates consist of
lead grids cast in suitable moulds. Each plate is composed of
two grids riveted together with their respective openings
flared inwardly, so that the active material is thus locked in
place (Figs. 147 and 148). The square openings in the negative
plates are filled with a paste of litharge, and in the positive
plates with one of minium. The current reduces the litharge
and peroxidizes the minium.

Faure-Sellon-Volckmar Accumulator (New System).—The
grid of this accumulator (Fig. 149) is made of an alloy of lead
and antimony, and the openings, which are bevelled out-
wardly as shown in Fig. 149, are packed with lead peroxide, as
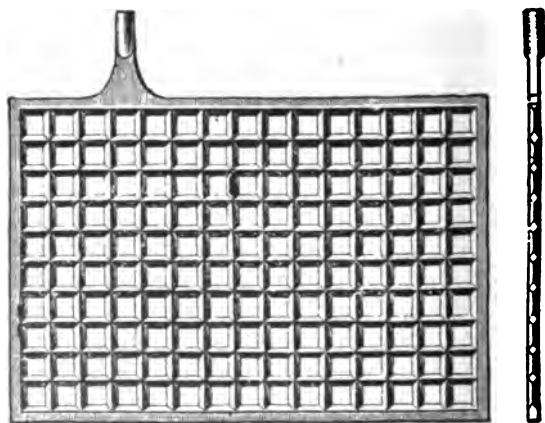
FIG. 149.—FAURE-SELLON-VOLCKMAR GRID.

represented in Fig. 150. The grids are then placed in a
wooden vessel coated within with a substance not attackable
by sulphuric acid. The advantages claimed for the special
construction shown are that the active material cannot be-
come detached from the grids, and the almost complete con-

tact of the active material with the liquids over the surface of the plate reduces resistance.
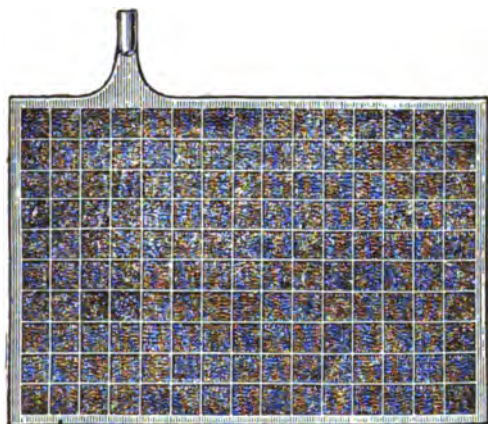
FIG. 150.—FAURE-SELLON-VOLCKMAR FILLED PLATE.

Philippart Bros. Accumulator (1888).—The plates are of the Faure-Sellon-Volckmar system, but their construction is different. They are connected in pairs, as shown in Fig. 151, each
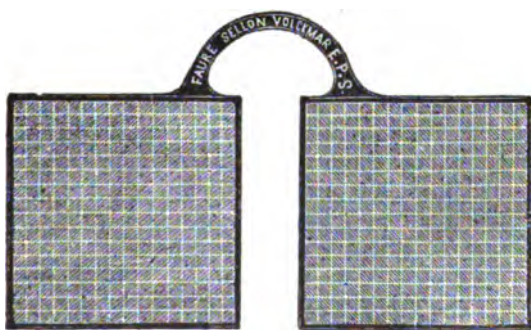
FIG. 151.—PHILIPPART ACCUMULATOR PLATES.

pair consisting of a positive and a negative plate joined by a bridge-piece of an alloy of lead and antimony. The receiving vessels are placed side by side. In vessel No. 1 are disposed the extreme positive plates of the battery all joined to one
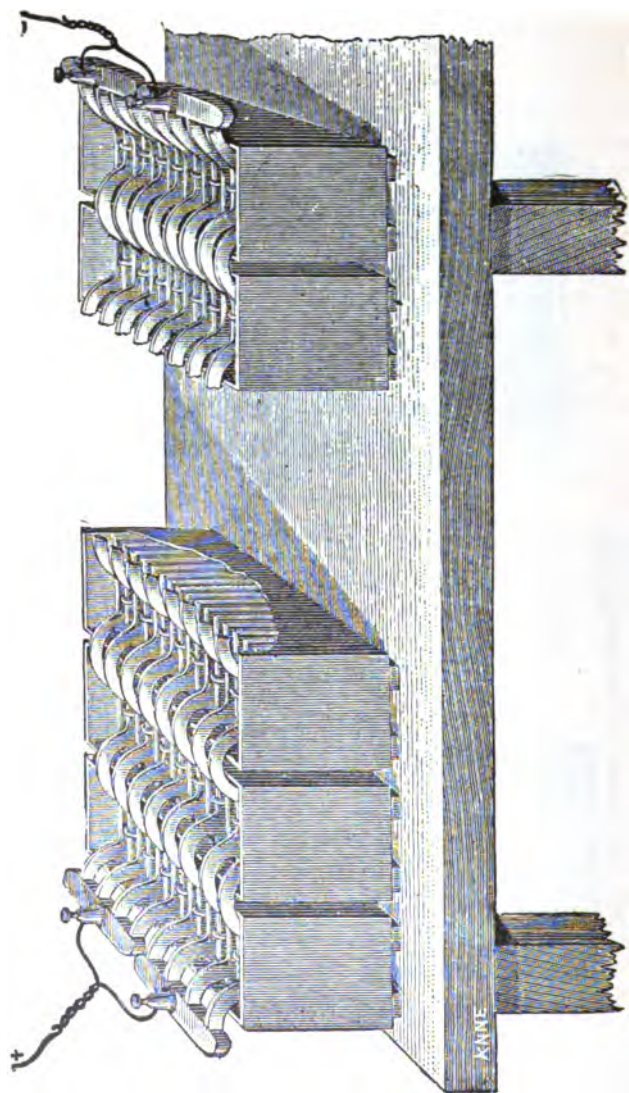
FIG. 152.—PHILIPPART ACCUMULATOR.

main terminal. Alternating with these are the negative plates, which are connected by their bridge-pieces with the positive plates in receiving vessel No. 2. The negative plates in vessel No. 2 are connected by their bridge-pieces with the positive plates of No. 3, and these last may be united to a common terminal. This arrangement will readily be understood from Fig. 152. The individual plates are kept apart by glass riders received on their upper edges and extending down between them. The principal advantages claimed are the independence of the plates and the absence of joints and soldering.

Julien Accumulator.—The grid electrodes consist of an alloy of lead 92 per cent, antimony 3.5 per cent, and mercury

FIG. 153.—JULIEN ACCUMULATOR.

4.5 per cent. Minium is compressed in the openings of the positive and litharge in those of the negative electrode.

The apparatus for filling the Julien plates is a hydraulic press obtaining its pressure from a pump driven by a belt and pulley. The plate to be filled with active material is placed in a die, which forms the top of the piston-plunger of the hydraulic press. The active material, placed above and below the plate
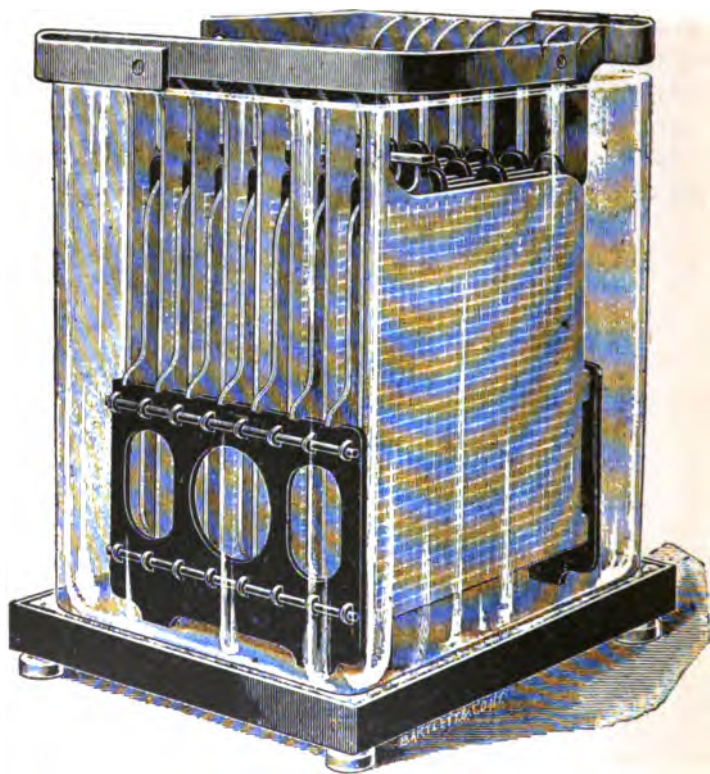
Fig. 154.—Electrical Accumulator Co. Accumulator.

in the form of dry powder, is then brought up by the press against the opposite head, and the active material is then forced into the grid, so as to form a solid and compact mass. This operation takes place in less time than is required to describe it. Thus one of these machines with two boys will fill 2000 plates per day, and hence replaces the work of

tnirty skilled men, which would be required under the old
method of pasting in the active material by hand.

The standard type of electric lighting and power cell, known
as the S 17 accumulator, is shown in the illustration on page
441. It has 180 ampere-hours capacity, and its maximum
charging rate is 15 amperes, and discharging 20 amperes.
It occupies a floor-space 7 × 8 × 10 inches high, and weighs,
complete, set up with acid, 42 pounds.

The Electrical Accumulator Company's Accumulator.—This
is made of different sizes and a variable number of plates,
according to the purpose for which it is intended. The
standard type shown, Fig. 154, made by the Accumulator Com-
pany of New York, has fifteen plates, seven positives and eight
negatives, those plates being called positive which are con-
nected with the positive pole in charging and from which the
external current flows in discharging; the others being known
as negative. Each positive plate is $9\frac{1}{8}$ in. high, $8\frac{1}{2}$ in. wide,
and $\frac{1}{4}$ in. thick; and each negative $9\frac{7}{8}$ in. high, $9\frac{1}{2}$ in. wide, and
$\frac{3}{16}$ in. thick. They are of lead cast in the form of grids, with
square openings to hold the paste. (Fig. 155.)

Each opening is $\frac{5}{8}$ in. square at the surfaces, but smaller in
the centre, the walls being thicker, sloping inward from each
surface as shown in cross-section at B, Fig. 155, an improvement
by Sellon to prevent the paste from falling out. These open-
ings are filled with the paste of lead oxide
and sulphuric acid ; minium, Pb_3O_4, being
used for the positive plates, and litharge,
PbO, for the negatives. From one of
the upper corners of each plate a lead
bar extends as shown in Fig. 155. It is $\frac{5}{8}$
in. wide, the same thickness as the plate,
and extends $2\frac{5}{8}$ in. above the highest
plates. These vertical bars on each set
of plates are attached to a horizontal bar
of the same width, as shown in Fig. 154,

FIG. 155.—GRID.

connecting the set of plates together and keeping them a given
distance apart, the space between each two positives being
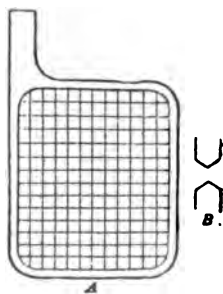
$\frac{9}{16}$ in. and that between each two negatives $\frac{5}{8}$ in., each set with its bars being a single casting. The horizontal bars are extended and the ends turned in for convenience, forming lugs for connecting the cells into a battery (see Fig. 154). When the plates are ready to be set up, the seven positives are passed in between the eight negatives, so that they alternate, each positive being between two negatives with a $\frac{1}{16}$-in. space between them. In Fig. 154 the positives are shown with their bars to the right, and the negatives with their bars to the left. As the outside plates are negatives and the outside surfaces inactive, the same number of active surfaces, positive and negative, fourteen in each set, are adjacent to each other within. In each negative plate a number of openings are left without paste, into which are drawn plugs of soft rubber, which project $\frac{3}{16}$ in. on each side, resting against the positives and holding the plates that distance apart. Two plates of glass of the same size as the lead plates are placed outside, one on each side, against the projecting rubber plugs, to keep them from being pressed out, and all the plates are bound together and held in position by strong rubber bands. They are then placed in a glass jar 11 in. long, 8½ in. wide, and 13 in. high outside, and rest on two strips of wood placed in the bottom to allow

LIST OF ELECTRICAL ACCUMULATOR COMPANY'S STANDARD CELLS.

(APPROXIMATE DATA.)

Type of Cells.	Charging Current.	Working Rate and Capacity, Amperes.				External Dimensions of Jars, Inches.						Weight of Acid, lbs.		Weight Complete Cell, lbs.		Height over all, including Connections.
	Normal.	Normal.		Maximum.		Glass.			Rubber.			Glass.	Rubber.	Glass.	Rubber.	
	Ampere.	Rate.	Ampere-hours.	Rate.	Ampere-hours.	Length.	Width.	Height.	Length.	Width.	Height.					In.
15 L.	15 to 30	30	300	40	250	10⅜	12¼	13⅜	....	....	....	50	....	130	....	15½
23 M.	10 to 25	25	150	30	110	10½	8¼	9½	6⅜	7¼	9½	16	11	50	40	11¼
15 M.	5 to 15	15	100	20	70	7½	8¼	9½	4¼	7¼	9⅞	11	7	35	25	11¼
7 M.	2 to 6	6	40	8	25	4¼	8½	9½	2¼	7½	9½	6	3¼	20	13	11¼
5 S.	1 to 2	2	8	3	6	....	....	....	1¼	3½	6¼	....	¼	....	2¼	7

Electromotive force of each cell is about 2 volts.

free circulation of the fluid. The average E. M. F. of this. cell is about 2 volts, its internal resistance .005 ohm, and its. capacity 350 ampere-hours, its best working rate being 35 amperes for 10 hours. The cell weighs 125 lbs., which can be reduced by using $\frac{1}{8}$-in. and $\frac{3}{32}$-in. plates, but it is not so durable.

The table opposite gives the particulars of standard " Accumulator " cells.

Peyrussch Accumulator.—The lead support is composed of a central rod and a number of longitudinal and radial strips, which are placed in a porous cup. The spaces between the strips are then filled with peroxide of lead and other material capable of producing the same by oxidation, which is mixed with a little acidulated water. Other forms may be substituted for the radial strips. The porous cup is placed in a second vessel of glass, containing the negative electrode.

Schoop Accumulator (Fig. 156).—This has a gelatinous electrolyte made by adding one volume of dilute sodium silicate (water-glass), density 1.18, to two volumes of dilute sulphuric acid of 1.250 density. To
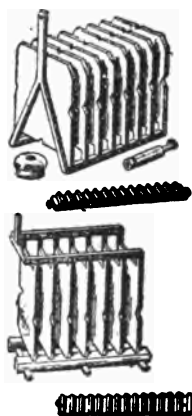
FIG. 156.—SCHOOP ACCUMULATOR.

prevent short-circuiting between the plates by the material dislodged in working, they are either slung or rested on supports which are so placed that the formation of a layer of mud between them is prevented.

Tudor Accumulator (Fig. 157).—The positive plates are first treated by Planté's process, coating them with a layer

FIG. 157.—TUDOR ELECTRODE.

of crystalline electrolytic peroxide; the grooves are then partially filled with a paste of peroxide of lead, and pressure is applied to the ridges to expand them and partially close the mouths of the grooves.
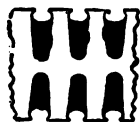
Besides the improvements in the plates, various devices have been resorted to with the view of decreasing the resistance of the lugs and securing better contact

between plates of the same sign, such as making connection
by tinned copper rods passed through holes in the lugs.   Lead
is afterwards cast around the copper so that it is screened from
the action of the acid.

Tommasi Multitubular Accumulator (Fig. 158), invented
by Dr. Donato Tommasi, of Paris, has each electrode formed

of a perforated tube, or folded sheet,
closed at one end by a small plate
of insulating material, into which is
screwed a rod.   The rod, which serves
as a support for the tube electrode,
is provided with a suspension-head,
which also serves as a contact.   In-
stead of cylindrical tubes, prismatic
ones may be employed, as in Fig. 158,
utilizing the space to better advan-
tage.   In the annular space between
the tube and the contact conductor of
each electrode the active material,
spongy lead, or lead oxide, etc., is

FIG. 158.—TOMMASI ACCUMULATOR.   packed, so that the tube serves only as
a support for such matter, and can be made of any substance
desired, so long as it is not attacked by the acid.   The charg-
ing current varies from 1 to 4 amperes per kilogram of plates,
and the discharge from 1 to 3 amperes.   The available capacity
in ampere-hours, under a discharge of 1 to 3 amperes per
kilogram, is 20 ampere-hours per kilogram.

Kornbluh Accumulator.—Each electrode is a lead plate
with openings in which minium is compressed.

Somzée Accumulator (1883).—Cellular plates having pockets
which, when the plates are put together, form a cavity for the
reception of lead oxide.

Farbackg and Schenck Accumulator.—Lead grid electrodes.
The negative plate is packed with a paste of 95% lead oxide
and 5% pumice-stone wet with a 25% solution of sulphuric
acid.   In the positive plate is a paste of 47% lead oxide, 48%

minium, 5% coke in small grains wet with same solution. The plates are dried before use.

Brush Accumulator.—Electrodes of lead having grooves filled with electrolytic spongy lead, or with lead sulphate made into a paste with water. The sulphate plates are afterwards placed horizontally in a vessel containing a solution of any salt in which lead sulphate is soluble. A zinc plate is suspended in the solution above each lead plate. On current being established the lead sulphate is reduced to spongy metal, and the latter, when the electrodes are immersed in diluted sulphuric acid in the containing cells, is transformed into peroxide.

Nolf Accumulator (1883).—Lead plates covered with minium in a potash or soda solution. The solution is claimed continually to renew itself.

P. Gadot Accumulator (1888).—The plates, as shown in Fig. 159, are made double, each with flared openings, which unite to hold the active material (lead oxide). The following results of experiment with this accumulator have been obtained
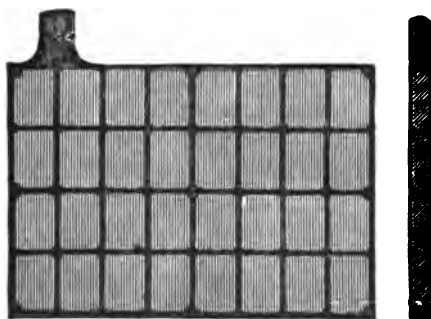
FIG. 159.—GADOT ACCUMULATOR PLATES.

by J. Laffargue. The battery contained ten negative and nine positive plates. The weight of active material was 7925 kg., and of inactive material (support) 8341 kg. The results were 225.7 utilizable ampere-hours, or 13.88 utilizable ampere-hours per kilogram of plates, represented by the curve shown on Fig. 160.

From experiments made on the Gadot accumulator by

Roux, an apparatus having 11 plates of 850 grams gave a
quantity efficiency of 85.2 per cent and an energy efficiency of
70.1 per cent.   In another experiment, where the weight of
plates was 9.35 kilograms charged at a constant difference of
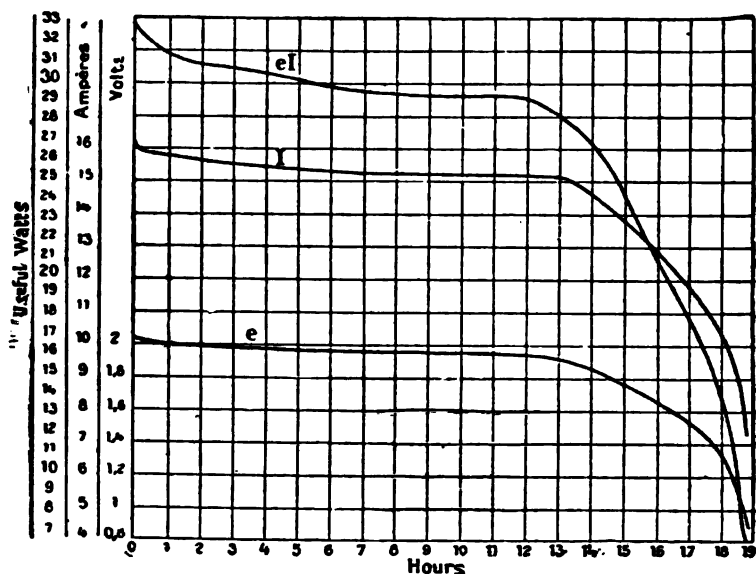
FIG. 160.—GADOT ACCUMULATION DIAGRAM.

potential of 2.28 volts and discharged on a constant resistance,
a quantity efficiency of 86.2 and an energy efficiency of 73 per
cent were obtained.

Winkler Accumulator (Fig. 161).—A series of celluloid
troughs in a frame of the same material.   Each trough con-
tains a metallic conducting wire embedded in active material,
the wires from the several troughs in each plate being con-
nected to a solid conductor which forms an electrode.   These
wires may be inserted before or after applying the active
material.   The open space between the bottom of each trough
and the active material of the trough below facilitates the
circulation of the electrolyte, and the escape of gases from the
active material is facilitated by the V shape of the troughs.

It is claimed that the celluloid supporting plates will not

buckle nor become deteriorated, and that a saving of from 40 to 50 per cent in the weight of the cell is effected.

FIG. 161.—WINKLER ACCUMULATOR GRID.

Jarriant Accumulator (1888).—The plates are of hardened lead 3.5 mm. in thickness, divided rectangularly by four strengthening ribs as shown in Fig. 162. The recesses are lozenge-shaped and are filled with minium made into a paste
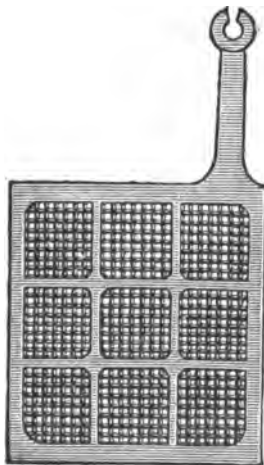
FIG. 162 —JARRIANT ACCUMULATOR PLATE.

with a 20% solution of sulphuric acid. Each lead plate weighs 810 grams and contains 400 grams of minium. The normal

battery has 29 plates held between two wooden supports. Bands of rubber are used to maintain the intervals of separation, which is about 7.5 mm. between faces of adjacent plates
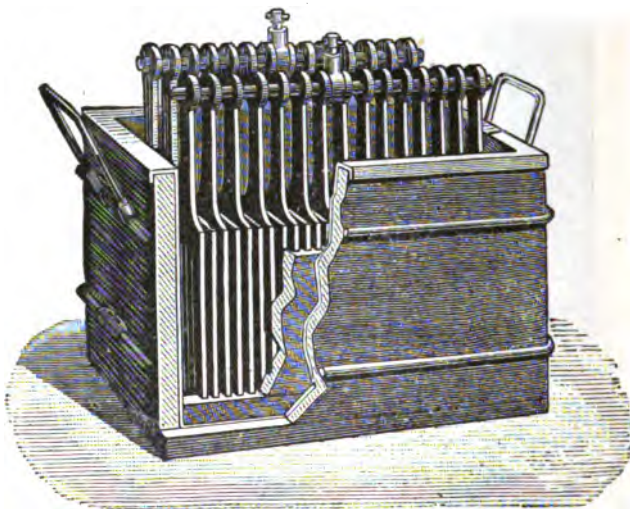
FIG. 163.—JARRIANT ACCUMULATOR.

(Fig. 163). The liquid is a 12% solution of sulphuric acid. The total weight of the 29 plates is 35 kg., and the battery
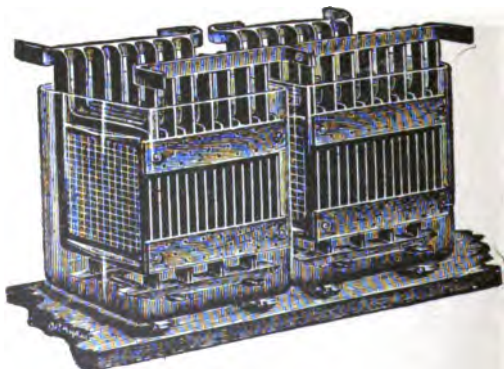
FIG. 164.—DRAKE AND GORHAM ACCUMULATOR.

suitably charged gives on discharge a utilizable current of 64.7 watt-hours, or a yield of more than 76%.

Drake and Gorham Accumulator (1888).—The electrodes are grids of lead alloy filled with a mixture of lead oxide (Fig. 164). It is similar to the E. P. S. accumulator.

E. P. S. Accumulator.—This cell, made by the Electrical Power Storage Company (England), has been constructed in numerous forms. A late type is represented in Fig. 165.
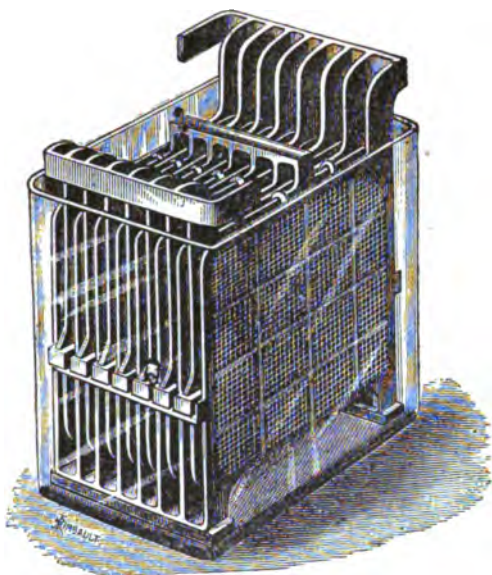
FIG. 165.—E. P. S. ACCUMULATOR.

The grid is made of lead and antimony and measures about $8\frac{1}{2} \times 9\frac{1}{2}$ inches in area, $\frac{3}{16}$ inch in thickness, and in weight about 5 lbs. Each battery has from 15 to 23 plates, of which from 7 to 11 form the positive electrode, and the remainder the negative. The active material is packed in the grids in the form of a paste. The following table gives the particulars of certain of these cells:

Elwell-Parker Accumulator.—The form of cell supplied by Elwell-Parker differs in several details from the E. P. S. pattern, though it is of the same type. The plates are held together by side frames of wood or vulcanite at the edges, so as

No. of Plates.	Material of Box.	Acid 1.770 sp. gr. for each Cell.	Charge, Amperes.	Discharge, Amperes.	Ampere hours.	Length.	Width.	Height.	Height over all.	Weight of Cell complete with Acid.
	Description of Cell.		**Working Rate.**		**Capacity.**	**Approximate External Dimensions.**				
		lbs.								
15 {	Teak	35	25 to 30	1 to 30	330	9½	13½	18¼	20½	143
	Glass	47	25 to 30	1 to 30	330	9⅝	11¾	13⅝	15¼	128
23 {	Teak	53	38 to 46	1 to 46	500	14¾	13½	18¼	20½	228
	Glass	67	38 to 46	1 to 46	500	14¼	11¾	13¾	15⅞	211
19 {	Teak	14	24 to 28	1 to 30	95	8¾	8¼	11⅝	13¼	52
	Ebonite	14	24 to 28	1 to 30	95	8	7¼	11	12¾	42
23 {	Teak	22	38 to 42	1 to 50	145	13¼	8¼	11¾	13⅝	80
	Ebonite	22	38 to 42	1 to 50	145	12¼	7¾	11	12¾	66

to knit them together very firmly and prevent buckling. The whole frame of the largest size can be lifted in and out by a crane with ease. The negative plates are made in a way which
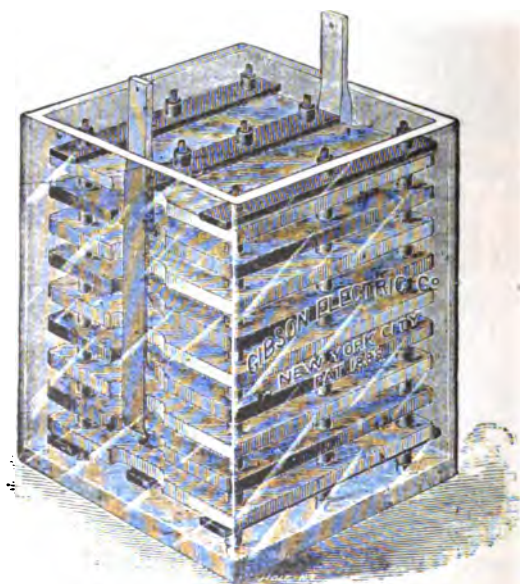
FIG. 166.—GIBSON ACCUMULATOR.

prevents blistering, a defect in the E. P. S. plates, and the grids are burred in a way which prevents the pellets from dropping out.

Gibson Accumulator (Fig. 166).—The peroxide of lead is introduced in capsules which are perforated, to allow the air to pass out when they are being filled, and also to permit the entrance of the electrolyte when the plate is immersed. The

FIG. 167.—PUMPELLY ACCUMULATOR.

capsules when inserted in the holes of the plate fit loosely and project beyond the surface. The plate is then rolled, and the pressure " upsets " the capsules and compresses them against the adjacent metal. The plates are arranged horizontally, are strung on bolts, and have distance-pieces between them to keep them apart and prevent short-circuiting.

A 75-ampere-hour cell weighs 29 lbs. complete, and a 175-hour cell 55 lbs.

Pumpelly Accumulator (Fig. 167). This also has horizontal plates. They are cast of a composite metal of the gridiron form, and are perforated to hold the minium. They are insulated by rings of pure rubber, and between each pair of plates there is placed a sheet of asbestos cloth. If any peroxide falls, it is caught by the asbestos cloth and cannot cause a short circuit. At one end of each plate is a hub covered with rubber, into which the plate of the same kind above it fits snugly, and through all of them is threaded a copper conducting rod, which is coated with lead to protect it from the acid. The standard cell illustrated is composed of 11 positive and 12 negative plates, each $6\frac{1}{4}$ and $6\frac{1}{2}$ inches, placed in a vulcanite case, $8 \times 8 \times 10$
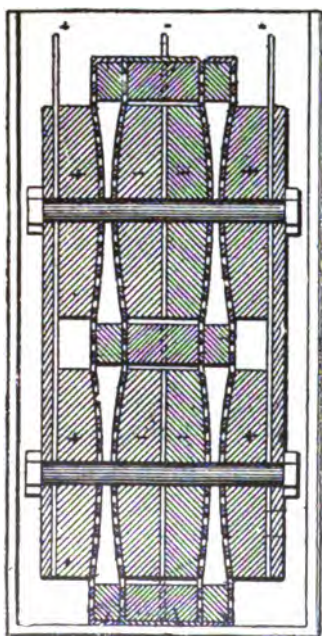
FIG. 168.—HERING PLATE.

FIG. 169.—HERING ACCUMULATOR.

inches. The whole weighs 32 pounds, and is claimed to have a working capacity of 240 ampere-hours, with an economic discharge rate of 25 amperes. The internal resistance in discharge is .003 ohm.

Hering Accumulator (Fig. 168).—In this form of accumulator, devised by Mr. Carl Hering, the two outer plates

are solid blocks of lead peroxide, such as may be made by mixing lead oxide in a solution of salts of lead, pressing the mixture in a mould and forming it into the shape desired. The two inner blocks are of spongy lead. These blocks of lead and peroxide are not fastened permanently to any electrode; they are simply held in contact with the contact-plates of lead or lead alloy, which lie against the flat sides of the blocks of active material and project as shown through the top of the cell. The means taken to secure proper contact are simple. Perforated straps of non-conducting material pass, as shown, over the exposed surfaces of both positive and negative plates, keeping the plates firmly in contact with the removable electrodes and at the same time keeping them apart from each other.

Fig. 169 shows the Atlas cell devised by Mr. Hering, in which the blocks of oxides and salts of lead are disposed horizontally.

Knowles Accumulator (Figs. 170, 171).—The plate is made
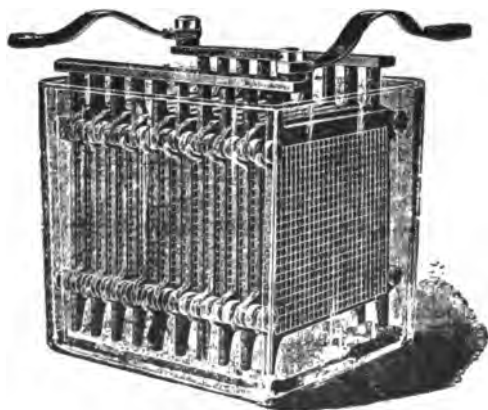
FIG. 170.—KNOWLES ACCUMULATOR.

in halves, one of which is cast with feet and the connecting lug. The other plate is cast with the hooks and with edges which, when the plates are put together, are folded over, as shown in Fig. 171, so as to bring the two into

intimate connection. Between the plates thus formed there is placed the active material in the form of a plate. The active material is compressed separately in a special mould, and is made to fit snugly between the two walls of metal thus prepared for it. The whole is bound together by means of rivets, which pass through the five holes in the plates. The latter
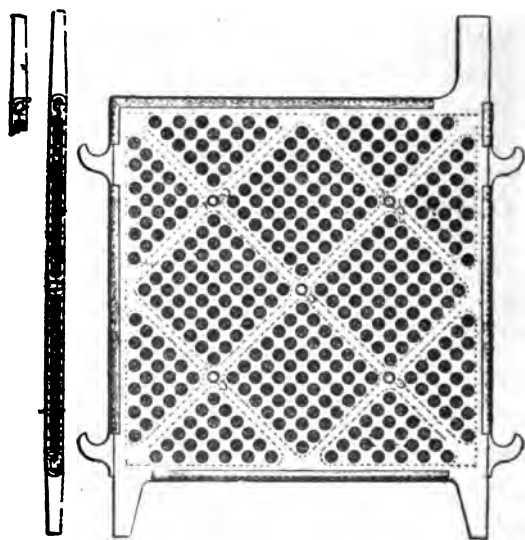
FIG. 171.—KNOWLES ACCUMULATOR.

are perforated, and are cast of an inoxidizable alloy. When the plates and active material are assembled they are held in position by flexible insulating rods passing through the hooks cast on the alternate plates and pointing in opposite directions.

Eickemeyer Accumulator (Fig. 172).—The cell consists of a flat cast-lead plate foundation, A, provided with a number of holes, a, polygonal in form. These openings a are lined with the active material, b, which is well packed around plugs, which, when removed, leave the central openings c. Each plate has a projecting terminal, d, and all are counterparts cast from the same pattern, so that when reversed in position and piled one on another with the terminals located alternately on opposite

sides, the holes *c* register with corresponding holes in all the plates throughout the pile. Between each two plates there is placed an insulating plate, *B*, which is also provided with holes, *e*, corresponding to those in the lead plates.
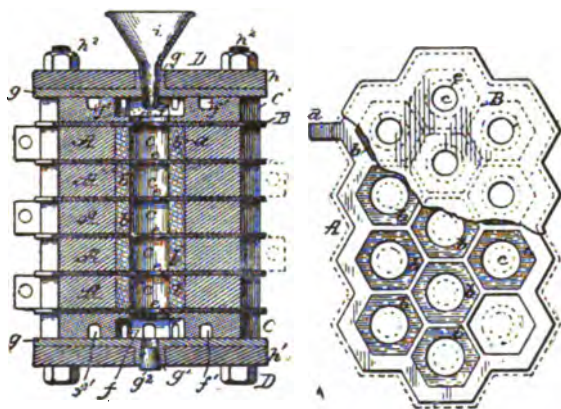
FIG. 172.—EICHEMEYER ACCUMULATOR.

With the battery thus constructed each vertical line of holes *c* constitutes a cell or chamber for containing the electrolyte, and this is supplied by means of a stand-pipe or funnel, *i*, which tightly fits the feed-aperture, *g'*, at the top, the lower central sleeved hole, *g'*, being meantime stopped by a rubber plug, *g'*. As the liquid falls to the bottom of the battery it is distributed by way of the lower channels and openings, *f' f'*, in the base-plate *C* to the several cells, in which it rises with uniformity until all are properly filled.

Reckenzaun Accumulator (Fig. 173).—The active material is completely formed in advance of its application, and is so held in place that the expansion of the plate has no effect on the adhesive property of the active material. Small cylinders of peroxide of lead are prepared, and placed at short distances from each other in regular lines upon the lower half of the corrugated mould. The two halves being fitted together, the molten metal is poured in, forming a composite plate.

These cylinders are exposed for a large part of their surface to the direct action of the electrolyte, being held only at the top.

But the enclosing metal is sufficient to permit the plate to be
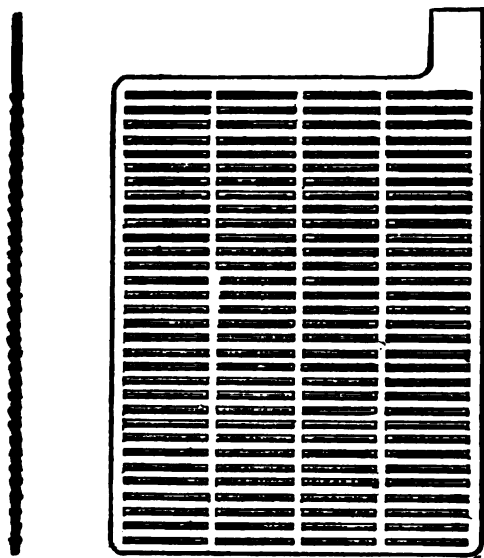
FIG. 173 —RECKENZAUN ACCUMULATOR PLATE.

bent over into a complete circle, without causing the small cylinders to fall out. The plates are designed specially for street-car and similar work, where rough treatment is unavoidable.

Detroit Accumulator (Figs. 174, 175).—The plates are made in the following way: A mould of the requisite size— say ten inches high, ten inches wide, and ten inches long—is filled with large crystals of common salt. Molten lead is then poured into the mould. The metal will, of course, readily penetrate the spaces between the crystals, which are embedded in the molten mass. When the mass cools it is sawed into disks of the desired thickness, and the plates are placed in water to dissolve the salt. When this has been accomplished the plates are full of irregular cavities of the form of the salt crystals. This appearance of a portion of the surface of the plate is shown in Fig. 175.

The active matter, minium, is put into the cavities. As the irregular spaces which had been occupied by the salt are larger
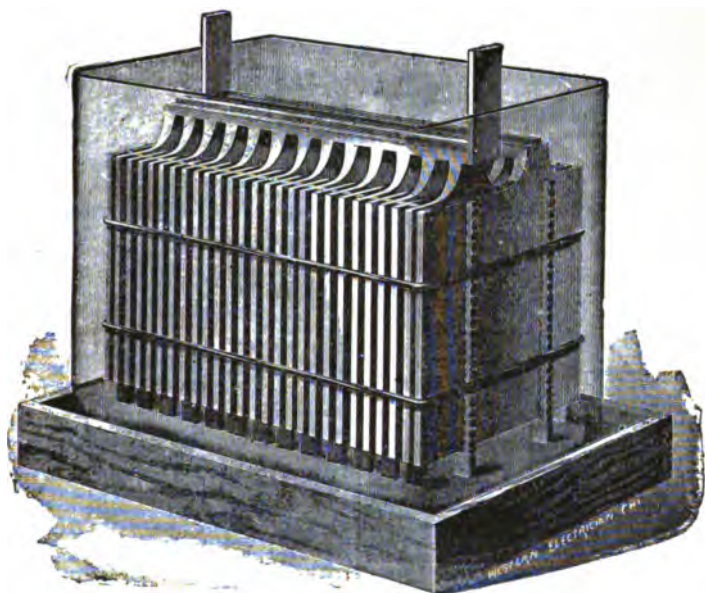
FIG. 174.—DETROIT ACCUMULATOR.

FIG. 175.—PORTION OF DETROIT ACCUMULATOR PLATE.

inside than outside, the active material cannot drop out. These plates are formed and connected in the usual way, and

the positive and negative electrodes are insulated from each other by hard-rubber dividers in the shape of corrugated forks. The closed end of the fork is put at the bottom; thus each plate is independently supported by two of these forks.

Brussels Société l'Electrique Accumulator.—The plates consist of hollow cones of lead, 30 centimetres in diameter, 20 centimetres high, and 3 millimetres thick. The external surface of each cone carries a number of projections, which serve the double purpose of supporting the active material and of keeping the cones apart. The internal surfaces are covered with litharge and the external surfaces with minium, and thus each cone plays the double *rôle* of positive and negative plate. The cones are mounted one inside another, and the spaces between them filled with sulphuric acid, the projections forming the contacts.

Sorley Accumulator (Fig. 176).—The plates of the cell are

FIG. 176.—SORLEY ACCUMULATOR PLATE.

built up of lead strips which are bent into the shape shown and united. The active material occupies the interstices left by the convolutions.

Macraeon Accumulator.—The negative plates are frames into which is cast a fused salt of lead, forming the active

material. The positive plates are made of strips of chemically pure lead which are " formed " by a special treatment involving electrolytic action in a bath containing nitrite of ethyl.

Acme Accumulator.—Each plate consists of a thin, slotted sheet of lead having a projecting tongue for making connection between adjacent plates. This thin sheet is then surrounded by the active material, which is held in place by grids made of insulating material which are placed on either side. The four holes shown at the corners of the grids serve for the insertion of the bolts which maintain the grids in position, and, passing through the successive elements, bind them all into a solid mass. Fig. 177 shows the grids and lead sheet taken apart.

FIG. 177.—ACME ACCUMULATOR GRIDS.

Ford-Washburn Accumulator (Fig. 178).—Six sets of electrodes are employed, the negative completely surrounding the positive and consisting of receptacles of especially prepared lead perforated to allow the acid to percolate readily. The holes are not sufficiently large, however, to permit any active material to force its way out. The positive electrodes consist of a porous pot containing active material surrounding a conducting medium of perforated lead so arranged as to compensate for expansion and contraction. The negative electrodes touch one another and are connected by a solid lead strip welded to
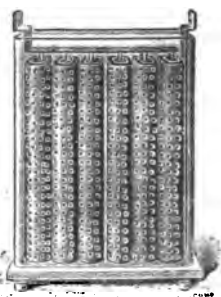
FIG. 178.—FORD-WASHBURN ACCUMULATOR.

all of them at the bottom, while the positive electrodes are sim-
ilarly connected at the top. By this arrangement an evenly
distributed discharge of extra strength is given to the battery.
The positive and negative electrodes are separated by the
porous partition one eighth of an inch thick.

Various Grids.—In addition to the forms of grids for
holding the active material which enters into the construction
of the accumulators above described, there are a large number
of special types, which are the main characteristics of the cells
in which they are found. In the *Correns Grid*, Fig. 180, much
used in Germany, the shape is that of a double lattice.

This grid seems to be cast by means of metallic moulds,
using the trick of placing the milling of the lower part of the

FIG. 179.—CORRENS GRID.

mould upwards and that of the upper part downwards. Fig.
179 gives an idea of the process, and Fig. 180 shows a grid with
some of the active material in place.

FIG. 180.—CORRENS GRID.

The positive and negative electrodes seem to be exactly
alike; the mode of connection of the plates to a section is
similar to that observed in the old-style E. P. S. cell. The
plates are perhaps one quarter of an inch thick, longer than

they are high, and are provided at the upper part with two projections for the purpose of suspension.

A variety of forms of grids of German make are represented in Figs. 181 to 186.

FIG. 181.   FIG. 182.   FIG. 183.
VARIOUS GRIDS.

Fig. 182 represents a grid for positive or negative plates.

Fig. 183 is a grid for both positive and negative electrodes for higher rates of charge and discharge for unit we:ght of cell.

FIG. 184.   FIG. 185.   FIG. 186.
VARIOUS GRIDS.

Fig. 184 seems good for small-sized plates, and for the highest possible rates of current. It seems especially adapted to train-lighting, electric launches, and power purposes.

Fig. 185 shows a piece of grid for large-sized plates, intended for use in batteries for lighting, and Fig. 186 is a piece of grid for largest size electrodes; this sample is a marvel of lead casting. It seems to consist of three separate grids, connected with each other by numerous cylindrical bolts, but the whole is made in one cast.

In the *Roberts* cell, Fig. 187, two grids are used, pasted on

the side and then united to form a plate with the paste inside by vulcanite bolts and nuts. The active material in expanding here pushes the grids apart without (it is said) bending or buckling them.
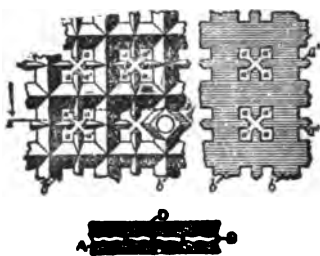
FIG. 187.—ROBERTS GRID.

Gardner's Grid is a series of superposed horizontal troughs packed with lead oxide. *The Pitken and Holden "Ladder" Plate* also consists of a series of shallow troughs arranged ladderwise in their supports and filled with lead oxide.

Drake and Gorham's Grid is an ordinary cast metal grid passed between rollers and burnished down on the outer edges on both sides of the plate. A sort of double dovetail is thus formed in each aperture.

Hagen's Frames are made of any of the alloys now used for holding the lead salts. They are constructed in halves with ribs crossing at right angles so as to leave square apertures. Each rib is in the form of a triangular prism with its base outwards. The halves are not cast solid along the inner angle of the ribs, but at some little distance apart, and are merely held together where the ribs cross by a series of short cross-bars.

Jacquet's Grid is a plate having double dovetailed apertures placed diagonally. One kilogram of plate contains 622 grams of active material. *Humphrey's Grid* is made in open lattice form by connecting the sides of the framework of each plate to bars either of a diagonal or an oval section, the bars being arranged like the slats in a Venetian blind.

Grid Rolling Machine.—A novel machine for rolling grids has been devised by Mr. A. F. Madden. His process

consists in rolling semi-fluid lead into a mould or "former" travelling back and forth under a roller, the grid being ejected at one end of the stroke. A turret contains the lead and apparatus for heating. From below this the lead is fed into an air-tight retort, closed at the bottom by a moving carriage containing the "former." When the "former" is under the retort, its movable divisions are lowered for the reception of the lead, which is then crushed into it by the roller, and a reverse action at the other end of the stroke lifts the plate out. An ingenious device is also provided for stacking the grids as they are delivered from the travelling carriage.

One feature of Mr. Madden's grid is the shape of the perforations, the divisions between which, instead of increasing in thickness from their outer edges inward, have the same thickness throughout except at the edges, where a slight "burr," made in the manner described above, assists in holding the active pellets in place. After the grids leave the automatic machine they are passed through another machine which closes the perforations several thousandths of an inch all around by a slight "burr," and at the same time hardens them. The machine is capable of turning out 5000 grids in ten hours, and is said to produce not only a grid of high mechanical perfection, but one of much tougher material than can be produced by casting.

CHAPTER XXII.

ACCUMULATORS. *(Continued.)*

III. BIMETALLIC ACCUMULATORS.

IN this type the electrodes consist of two different metals in an electrolytic fluid, which is a soluble salt of one of such metals, like the so-called zinc-lead accumulators, with electrodes of zinc and lead in sulphate of zinc, and the copper-lead accumulators, with electrodes of copper and lead in sulphate of copper. In this class the zinc and copper are alternately deposited and dissolved, and the lead oxidized to the peroxide and reduced to spongy lead. The history of such batteries, in their primary form, dates back many years. In 1826 Nobili deposited peroxide of lead upon platinum plates by the electrolysis of a solution of acetate of lead; and in 1837 Professor Schönbein of Basle announced that such plates possessed highly electro-negative qualities. De la Rive soon after, acting under this suggestion, experimented with the peroxides of lead and manganese, and constructed a battery in which peroxide of lead moistened with dilute sulphuric acid, and surrounding a plate of platinum, acted as the negative plate, and zinc in dilute acid as the positive. He obtained powerful results from this arrangement. Grove, soon after the invention of his gas battery in 1842, also experimented with the oxides of metals. In 1843 Wheatstone designed a battery in which the negative plate consisted of platinum, with peroxide of lead deposited upon its surface (by the electrolysis of a solution of acetate of lead), and the positive plate of potassium amalgam. This is the most energetic battery ever tried, but extremely

impracticable and expensive. Joule also used the peroxide of lead in the same manner, but the positive plate was amalgamated zinc in caustic potash. He obtained an electromotive force of 2.54 volts. The use of platinum was the great drawback, besides which, as soon as the peroxide of lead was reduced, it had to be renewed, as did also the zinc when consumed. This style of battery has been little used, with the exception of the well-known Leclanché cell, similar in nature but containing peroxide of manganese instead of peroxide of lead. In the Planté forms there must be a positive plate of a fixed size in order to get the best results, but in the bimetallic forms even a small stick of zinc can be used, as it is alternately dissolved and deposited. Mr. G. H. Percival, in 1869, described such a battery, and the action was supposed to be as follows : Electrodes of zinc and lead being in sulphate of zinc, a current of electricity is sent through the battery, entering by the lead plate. The sulphate of zinc by electrolysis splits into zinc and the radical SO_4. The zinc is deposited upon the zinc plate, but SO_4 splits into anhydrous sulphuric acid (SO_3) and oxygen (O). The oxygen attracts the lead plate and, the oxide of lead being insoluble, peroxide of lead is formed (SO_3), joining with one molecule of water to form sulphuric acid, or $SO_3 + H_2O = H_2SO_4$. This liberation of free acid was the objection to this form of battery, as it rapidly reacted upon the deposited zinc, even when well amalgamated, hydrogen gas being given off, and there being in consequence a great loss of energy.

Sutton saw this objection, and used copper and lead in sulphate of copper. In this case the deposited copper was not attacked by the liberated sulphuric acid, but the action continued until all the copper was taken up from the solution, which was shown by its loss of color. This cell has a comparatively low electromotive force and varying resistance, there being good-conducting free acid at beginning of discharge, rapidly changing to the much more resisting sulphate of copper. This varying battery resistance is found also in Percival's battery, as also in all single-liquid salt batteries. D'Arsonval, in 1879, used carbon plates covered with the

peroxides of lead and manganese, and zinc in sulphate of zinc. This battery was open to the objection of free acid, which would condemn it, without taking into consideration the formation of sulphate of lead and disintegration of the carbon. plate. W. E. Case has attempted to overcome the liberation of free acid, by placing in the solution of sulphate of zinc enough magnesia to neutralize it as it is formed (Hogg. 1886).

Commelin, Des Mazures, and Baiihache (C. D. B) Accumulator.—The positive electrodes are porous copper plates obtained by the compression of copper dust under a pressure of 9000 pounds per square inch. The dust is obtained by the electrolytic reduction of copper scales in a bath of caustic soda. The plates are arranged in a copper frame. The negative electrodes are made of amalgamated tinned cloth of iron wire. The tin holds the mercury. The cell is made of tinned sheet steel held together by a system of hooking, and rendered water-tight before the tinning so that no leakage can occur through the attack on the tin. This tank is connected with the negative electrodes which rest on the bottom. The particles of electrolyzed zinc which fall down then again enter the circuit. The liquid consists of water 1000 parts, zinc 144.67, combined potash 200.82, and free potash 313.72. The positive electrodes are enclosed in parchment-paper cells and are supported by glass insulating rods. According to M. Findt, the reaction corresponding to the discharge is as follows :

$$Zn + KO, HOAq + Cu_2O = ZnO, KOAq + 2Cu + HO.$$
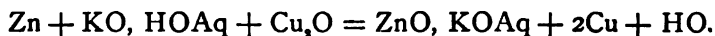
The application of this battery to a torpedo-boat of the French navy in 1887–8 gave the following results :

Weight of accumulators corresponding to 1 horse-power hour work = 37 kilograms.

Weight of accumulator corresponding to 1 horse-power = 170 kilograms.

These experiments showed that the efficiency of the alkaline battery was practically the same as that of a lead battery,

while its weight could be easily reduced to a point unap-
proachable by any practicable form of the old accumulator.
The weight of the alkaline accumulator per horse-power hour
proved to be from 55 to 60 pounds, and there was nothing like
the buckling that has proved so fatal to the positive plates of
ordinary storage batteries.

Waddell and Entz Accumulator (Fig. 188) is an improve-
ment upon the C. D. B. accumulator above described. The
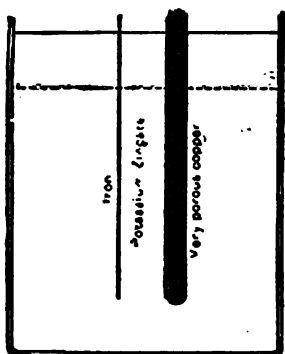
FIG. 188.—WADDELL AND ENTZ ACCUMULATOR.

copper electrode is made with a dense copper core surrounded
by exceedingly porous copper, and the whole enclosed in a
textile covering; the liquid is potassium zincate, and the
other electrode is of iron, permitting the deposition of the
zinc. As a matter of fact, numerous plates are employed in
each cell, just as in the ordinary lead battery, and the walls of
the cell itself are of iron and form a portion of the negative
pole.

It is claimed that this accumulator weighs only about 60
per cent of a lead battery of like capacity, and that it is ca-
pable of delivering 300 amperes without evolution of gas or
serious heating. To avoid the lack of coherence in pure
copper oxide, Messrs. Entz and Phillips have modified the
composition by combining with the oxide of copper a small
portion of sulphur and then heating the mixture. The sulphur
is thoroughly mixed with the oxide and then applied to the

woven copper wire. The whole is then heated to burn off the sulphur, but in so doing the oxygen of the copper is absorbed to form the SO_2, leaving the oxide in a reduced state on the support. The heating then being continued, the exposed portions of the particles of the mass are reoxidized, while the unexposed portions at the juncture, being protected from the air, remain metallic and serve to hold the mass together. The sulphur, when used in this manner, therefore acts as a binding, toughening, or hardening agent, without being actually. present in the mass after the treatment.

Faure Accumulator.—The active materials consist of finely divided metals, compressed together and enclosed in a case of asbestos about o o4 inch thick. This casing is, however, prepared before use by soaking it in a solution of barium chloride or of common salt, and then transferring it to a solution of a soluble silicate, which forms with the barium or sodium chloride an insoluble compound. The elements, prepared as indicated, are placed on some electrolyte capable of forming on electrolysis an insoluble compound with one or other of the two elements. With zinc and copper electrodes M. Faure employs potassium phosphate as the electrolyte, and the cell is " formed " by passing a current through it in such a direction that insoluble phosphate of copper is produced by combination with the copper electrode. This done, the spent liquor is thrown away, and a fresh supply of potassium phosphate substituted, after which the cell is ready for work. On closing the circuit, the phosphoric acid is transferred to the zinc element, the phosphate of copper being reduced to metallic copper again, and zinc phosphate formed. When run down, the battery can be recharged by a current in the opposite sense, which will again produce copper phosphate and reduce the zinc. The "forming" process could theoretically be dispensed with by employing phosphate of copper at first hand, but this material is difficult to prepare and manipulate.

Main Accumulator (1891).—The positive electrode consists of five lead plates connected by a cross-bar, also of lead, to which terminals are secured to connect with the

negative electrode of the adjoining cell. Each of these plates is made of a number of thin sheets of lead, enclosed between two stout outer sheets. These are all perforated simultaneously in a press and secured together by numerous leaden rivets. Sometimes, as shown in the illustration, there is also a centre sheet of the thicker lead.

The plates built up in this manner are then "formed" by the prolonged action of a charging current, which converts the
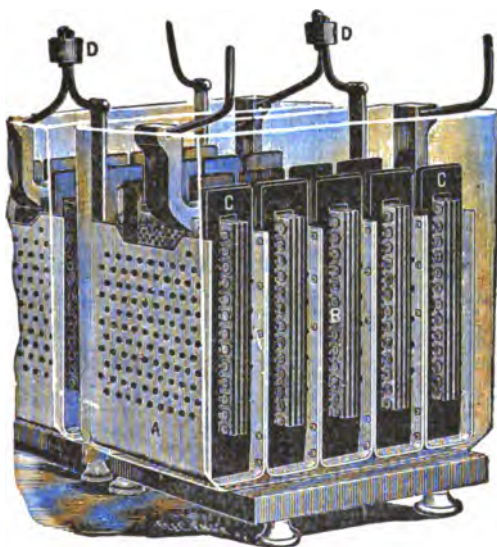
FIG. 189.—MAIN ACCUMULATOR.

thinner inside sheets completely into peroxide of lead, leaving the thick ones, which are but superficially affected, as permanent retaining walls and supports. The transverse holes which remain open give free access of current and fluid to the interior of the plate. Each plate is a little over 6 in. square and is claimed to yield 100 watt-hours under a moderate rate of discharge. The negative electrode is an amalgam of zinc and mercury deposited electrolytically upon a copper plate. The copper sheets are of No. 22 gauge, but the deposited zinc amalgam, with which they are coated, alters their form but

very little, although, of course, making them somewhat thicker and rougher than they would be otherwise. Each copper sheet has a number of large perforations through it, giving a better hold to the soft amalgam, and it is long enough to bend into a U form, so as to come opposite to both sides of the lead plate. These sheet copper U's are riveted together in numbers corresponding to the lead plates. A complete F 5 cell is shown in Fig. 189.

D'Arsonval Accumulator (1880).—The negative electrode is a plate of zinc; the positive electrode is a plate of carbon surrounded with finely granulated lead, and contained in a porous cup immersed in a concentrated solution of zinc sulphate. Under the action of the current the zinc salt is electrolyzed, zinc is deposited on the zinc plate, and the oxygen forms lead peroxide on the granulated lead.

E. Reynier Accumulator (1883).—The cell is barrel-shaped. The electrodes are a plate of lead of large surface peroxidized electrolytically, and a flexible lead plate in an acidulated solution of zinc sulphate. The last-named plate serves as a conductor, and also as a support for the zinc liberated by the charging current. E. M. F. = 2.37 volts. The commercial form No. 1 has three negative and four positive plates. Its constants are :

Surface of the four positive plates....... $= 200$ sq. dcm.
Weight   "   "   "   "   "   .... $= 8.200$ kg.
$E = $ E. M. F..................................... $= 2.37$ volts.
$R = $ average resistance................. $= 0.02$ ohm.
$I = $ normal intensity of discharge current $= 25$ amperes.
$i = $ "   "   " charge   " $= 5$ to 10 amperes.
$Q = $ accumulating capacity............. $= 550{,}000$ coulombs.
Total work per second, $\dfrac{EI}{g}$............. $= 5.7$ kgm.
Stored-up energy, $\dfrac{QE}{g}$................. $= 130{,}000$ kgm.

The chemical equation of discharge, according to Reynier, is

$$Zn + 2SO_4 + Aq + PbO_2 = SO_4Pb + Aq + SO_4Zn.$$
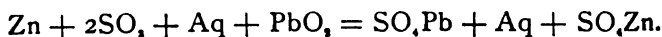
Reynier considers Aq. in this equation to indicate the in-dispensable intervention of water without prejudice to the number of molecules engaged (1, 2, 3, . . .).

The following are the constants of the Reynier commercial form No. 2:

Surface of positive electrode (lead)...... = 60 sq. dcm.
"   " negative electrodes (zinc)..... = 5 sq. dcm.
Weight of positive electrode............ = 2.200 kg.
"   " negative electrodes .... = 0.740 kg.
E. M. F.............................. = 2.37 volts.
Average resistance..................... = 0.06 ohm.
Normal intensity of discharge current.... = 5 to 7 amperes.
"   "   " charge   "   .... = 1 to 3   "
Accumulating ⎰ After 100 hrs. formation = 100,000 coulombs.
  capacity : ⎱   "   200 "   "   = 150,000   "

In another form of accumulator invented by Reynier a solution of copper sulphate instead of zinc sulphate is used. E. M. F. = 1.26 volts. The chemical equation is

$$Cu + 2SO_3 + Aq + PbO_2 = SO_4Pb + Aq + SO_4Cu.$$
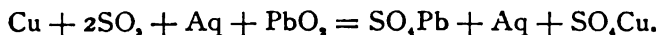
The constants are :

Surface of positive electrode (lead)...... = 60 sq. dcm.
"   " negative electrodes (copper).. = 5 sq. dcm.
Weight of positive electrode............ = 2.200 kg.
"   " negative electrodes.......... = 0.700 kg.
E. M. F .... = 1.26 volts.
Average resistance..................... = 0.06 ohm.
Normal intensity of discharge current... = 5 to 7 amperes.
"   "   " charge   "   .... = 1 to 3   "
Accumulating ⎰ After 100 hrs. formation = 100,000 coulombs.
  capacity : ⎱   "   200 "   "   = 150,000   "

Boettcher Accumulator (1883).—Zinc, peroxidized lead, zinc sulphate acidulated with acetic acid. E. M. F. = 2.5 volts.

Sutton Accumulator (1881).—Zinc, amalgamated lead, zinc sulphate solution. The inventor considers that amalgamated lead oxidizes more rapidly and much more uniformly than ordinary lead. In another accumulator devised by Sutton the negative electrode is of reduced copper; the positive, peroxidized lead; liquid, acidulated solution of copper sulphate. When this accumulator is charged, the copper sulphate is decomposed and the copper is deposited on the surface of the receptacle (which is of copper), while the oxygen, passing to the lead, combines therewith to transform the surface into lead peroxide.

Arnould and Tamine Accumulator.—The electrodes are alternate series of lead and copper wires; the liquid, a saturated and lightly acidulated solution of copper sulphate.

Rousse Accumulators.—(*a*) Plate of thin sheet iron and lead in a concentrated solution of ammonium sulphate.

(*b*) Plates of palladium and lead in a 10 per cent solution of sulphuric acid. Palladium absorbs over nine times its volume of hydrogen.

(*c*) Plates of thin sheet iron and lead, the latter coated with litharge or lead carbonate. The electrolyte is a concentrated solution of ammonium sulphate.

Sutton Accumulator.—Plates of iron and amalgamated lead in a solution of ferrous sulphate.

Hogg Accumulator.—This is intended to prevent the production of free acid. It consists of an electrode of zinc in sulphate of zinc of about 30° Baumé, and a porous cup containing an electrode of lead formed by the Parker-Elwell process, in dilute sulphuric acid. The action of the battery is as follows: the current enters by the lead electrode, the zinc sulphate is decomposed, zinc is liberated and deposited upon the zinc electrode, the radical SO_4 is liberated at the head electrode, but splits into SO_3 and O, the oxygen oxidizing the lead plate to PbO_2, and SO_3 joining with one molecule of water to form sulphuric acid, or $SO_3 + H_2O = H_2SO_4$. This acid is retained by the porous cup. The zinc is kept well amalgamated by a small quantity of bisulphate of mercury, and is but slightly

acted upon by the acid, which in time slowly leaks from the porous cup. Upon discharge, the sulphuric acid leaves the cup, attacks the zinc, forming sulphate of zinc, while the lead plate is reduced from the peroxide to lead oxide or spongy lead, as may be desired. The average resistance per cell is stated to be 0.25 ohm, and the E. M. F. between 2.3 and 2.0 volts. An efficiency of something over 60 per cent (under unfavorable conditions) has been obtained.

Laurent-Cely Accumulator.—This is distinctive in the special nature of the lead paste employed, and in the manner in which it is applied to the plates. The active element is a mixture of chloride of lead and chloride of zinc. The fused chloride of lead has a density of 5.6; by incorporating chloride of zinc with it in certain proportions the density is reduced to 4.5. This mixture, brought to a state of fusion, is run into cast-iron moulds in the form of small buttons with rounded edges. After cooling, the buttons are washed to remove the chloride of zinc, and to thus render them somewhat porous. Their density then varies from 4.2 to 3.4. The buttons which serve for the manufacture of the negative plates are then arranged in a metallic mould, into which antimonial lead is run; this surrounds the buttons with a frame which holds them fixed in their positions. The negative plates are mounted in cells filled with acidulated water and provided with zinc electrodes. The composite and zinc plates are then short-circuited. The hydrogen which is disengaged upon the positive electrode reduces the chloride of lead, and there are thus obtained buttons of spongy lead of a density between 2.5 and 3.1, while that of ordinary lead is 11.35. The buttons used in the manufacture of the positive plates are first transformed into spongy lead, then heated in the air to oxidize them, and transformed into spongy litharge. They are fixed, like the negative buttons, in a frame of antimonial lead.

IV. VARIOUS FORMS OF ACCUMULATORS.

Pilleux Accumulator.—Slightly concave plate of lead filled with a paste of lead sulphate acidulated with sulphuric acid, on

which is superposed another paste of lead oxide combined with vinegar. A canvas partition separates the two pastes.

Aron Accumulator (1882).—Plates of metal or carbon cov. ered with a paste formed of collodion and lead peroxide or finely divided lead.

Hatch Accumulator.—Metallic frames are not employed for supporting the active material, the lead salts being contained within the corrugations of a zigzag plate made of highly porous and open-grained earthenware. When the corrugations are filled so as to present a flat and even surface, a number of blocks are packed together, each adjacent pair of blocks being separated by a thin lead plate which acts simply as a conductor. On forming, the lead salts are converted into active material. The normal current efficiency of this accumulator (sometimes termed the " Cambridge" cell) is given as from 92 to 95 per cent, and its energy efficiency as 72 to 74 per cent.

James Accumulator.—The positive plates are of lead alloyed with one per cent of cadmium, and the negative plates lead alloyed with two per cent of antimony. The active matter is packed in circular holes in the plates. In the positive electrode it consists of minium litharge, asbestos, and carbon ; in the negative electrode of litharge sulphur, asbestos, and carbon.

Barber-Starkey Accumulator.—The inventor makes cells of the ordinary grid form mechanically solid by filling in the space between the plates with a dry mixture of sawdust and plaster of paris and then rendering it conductive by saturating it with dilute sulphuric acid.

Payen Accumulator (Fig. 191).—This has a porous crystallized metal plate, with the crystalline structure formed in columns with intervening cellular spaces.

To prepare the plate, a quantity of chloride of lead, for instance, is melted in a furnace, and a certain quantity of asbestos, or analogous material, is combined with it. When the mass has been thoroughly fused and mixed, it is discharged in a mould, in which it crystallizes on cooling. The plates

formed in this manner are then mounted together with lead plates into a cell, the system of crystallized chloride plates being connected to the negative pole of the dynamo. In the ensuing electrolytic action which takes place, the oxygen and chlorine are separated and caused to attack the system of lead
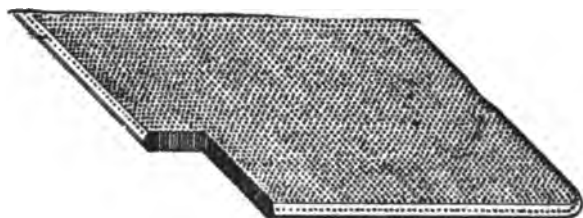
FIG. 190.—PAYEN ACCUMULATOR.

plates, while the crystallized plates are reduced to a metallic state, with the asbestos included as a binding material.

Heyl Accumulator (1891).—The electrodes are composed of combinations of plumbic, chromic, or tungstic acids with calcium, barium, or strontium. To increase the coefficient of output and capacity, the inventor uses more particularly compounds of calcium and lead, for the reason that there are easily oxidizable. The combination $CaPbO_4$, corresponding to 68 per cent of peroxide of lead, contains 4.56 per cent of active oxygen. The other alkaline earths, or of baryta, or strontium, furnish analogous compounds applicable to the purpose. Besides the advantage resulting from the chemical nature, the compound $CaPbO_4$ would offer a further valuable property in its porosity; it might replace the diaphragm employed to separate the elements of cells. The analogous compounds of chromium and tungsten can be employed in the same manner.

Kalischer Accumulator (1889).—Iron and lead in a concentrated solution of lead nitrate. The iron anode is passive, and with currents not too strong becomes coated with coherent thick layers of black peroxide of lead, which protect the iron from contact with the liquid and from decomposition. The change is completed when gas is freely liberated at the anode,

and the liquid gives only a slight precipitate with sulphuric acid. To prevent lead growths between anode and cathode, amalgamated lead in contact with mercury is used. In discharging, the peroxide becomes brown and changes into monoxide, then into black peroxide.● The electromotive force is from 2 to 2.5 volts, but sinks, when the current stops, to 1.8 volts. From its solubility in nitric acid the lead cathode must be occasionally replaced. Carbon can be used instead of iron.

Carbon Electrode Accumulators. — According to Mr. A. V. Meserole, carbon obtained from vegetable substances such as bamboo, boxwood, and the like, may be used as an active absorbent. It may be pulverized and mixed with variable proportions of graphite and pressed into porous pots or bags. The material should be worked into a paste with acidulated water, and then compressed within the porous retaining-envelope along with a number of conducting plates or rods composed of an alloy of lead and antimony amalgamated with mercury. The usual grid also may be filled in with this plastic material, and then closely wrapped with asbestos tape or cloth to prevent washing out.

Carrière Accumulator. — This has compressed carbon plates of either a plane or a corrugated, grooved or recessed surface, this surface being coated with a layer, from 1 to 1.5 millimetres in thickness, of a composition made by mixing litharge with dilute sulphuric acid containing $\frac{1}{10}$ of the strong acid. The carbon plates are manufactured by mixing two parts of pulverized retort-carbon with one part of lamp-black or of pulverized wood-charcoal, and forming these ingredients into a paste with a thin mixture of barley or wheat flour and water This mixture, after being moulded by compression, is dried in air, again pressed, subjected for some time to a temperature of 80° C., and lastly subjected for several hours to a temperature of from 1200° to 1300°, when they are allowed slowly to cool.

Tribe Accumulator (1883).—Electrodes of compressed lead peroxide.

Fitz Gerald Accumulator.—Positive plate, wholly of compressed lead peroxide; negative plate, an agglomerate of spongy lead. These electrodes are prepared by mixing litharge with chloride, sulphate, or chromate of ammonium. A cement is thus obtained which after a short time becomes firm and coherent. The best process consists in mixing lead oxide, pulverized metallic lead, and the solution of a salt which will be gradually decomposed by the oxide—as, for example, ammonium sulphate—while a certain proportion of lead oxide will be transformed into lead sulphate. This mass, converted by electrolysis into lead peroxide, is termed by the inventor "lithanode." The plates thus prepared are immersed in acidulated water and submitted to the current. The plates which are connected to the negative terminal are reduced:

$$PbO + H_2 = Pb + H_2O;$$
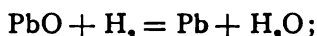
and these connected to the positive terminal are peroxidized:

$$PbO + O = PbO_2.$$
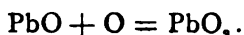
D. Tommasi Carbon Electrode Accumulator (1881).—The containing vessel is a wooden box lined with an insulating mastic, non-attackable by dilute sulphuric acid. The plates are of carbon agglomerate containing lead oxide. The liquid is 10 per cent solution of pure sulphuric acid. Charging is done in the ordinary way. The chemical reactions are:

At the positive electrode: $PbO + O = PbO_2.$

" " negative " $PbO + H_2 = H_2O + Pb.$

The advantages claimed are:

1. For the same volume, a weight from one fifth to one sixth that of lead accumulators;

2. A lead surface excessively large in proportion to the weight of the carbon plate;

3. Capacity of rapid formation.

Gardner Accumulator (1886).—Equal parts of powdered carbon and minium are combined, and to three parts of the

mixture are added one part of calcined magnesia. Of this a paste is made with mother-liquor from salt works, which paste is introduced into the cavities of the lead plates.

Epstein Accumulator.—Melted lead mixed with powdered manganese peroxide is brayed energetically until cool, thus producing a uniform small-grained powder. This with water forms a paste which is moulded into shape in a hydraulic press. In the plates thus formed are made grooves into which melted lead is run to form a support.

Barrier and Tourvieille Accumulator (1883).—Termed by its inventors the " Electrodock." Lead tubes threaded inside and outside are inserted one within the other, so that an interval is left between them. This space and the threads are filled with a special cement. Each tube is carried on the wooden cover which is common to all. The tubes are alternately connected and arranged in a vessel of glass or one made from the staves of petroleum-barrels. The cement used is composed of a mixture of litharge, powdered carbon, and potash permanganate ground together, sifted, and combined with glucose or sugar-sirup to form a paste, which is very solid and permanent even after the formation of the accumulator.

Tamine Accumulator.—The plates are agglomerates made as follows: 5 parts of melted resin or other agglutinant are combined with 20 parts of electrolytic lead peroxide and 75 parts of lead filings or pieces of lead in the shape of plates, wires, ribbons, etc. The mass is subjected to a pressure of about 300 atmospheres. The lead acts as conductor for the current throughout the plate, inserted in which also is a thick wire of lead which serves as a terminal.

Tamine has devised the following combinations:

Negative Electrode.	Positive Electrode.	Electrolyte.
Agglomerate plate, PbO_2	Agglomerate plate, PbO_2	Dilute sulph. acid
Zinc	" " "	Sol. zinc sulphate
Copper	" " "	Sol. copper sulphate
Agglomerate plate, PbO_2	Lead	Dilute sulph. acid
Carbon	Agglomerate plate, PbO_2	Sol. copper sulphate
Carbon	" " "	Sol. zinc sulphate
Agglomerate plate, PbO	Agglomerate plate, Pb_2O_4	Dilute sulph. acid

In this last combination, if it be desired that the formation on the two electrodes be exactly equal, the weight of the litharge, PbO, should be equal only to $\frac{2}{3}$ of the weight of the minium, Pb_3O_4.

Rousse Accumulator.—Plate of thin sheet iron, cylinder of ferro-manganese, and concentrated solution of ammonium sulphate.

Varley Accumulator.—Plates of carbon mercurized and plates of carbon covered with zinc amalgam immersed in a saturated solution of zinc sulphate to which sulphuric acid is added. By the action of the current, zinc is deposited in the carbon covered with zinc amalgam, and mercuric sulphate on the mercurized carbon.

Gimé Accumulator (1885).—A number of lead tubes perforated with longitudinal slits disposed in quincunx order and connected by metallic clamps. The tubes are filled with lead sulphate and are immersed in 10% acid solution. The claimed practical capacity is 3000 kgm. per kilogram of lead.

Regenerated Cells.—All chemical action reversible by electrolysis may produce a secondary couple, and hence an accumulator.

Thomson & Houston Cell.—Zinc-copper, solution of zinc sulphate. The zinc is placed at the upper and the copper at the bottom of the containing vessel. A porous diaphragm is below the upper plate, so as to prevent fragments of the zinc falling upon the copper. On charging a deposit of zinc takes place on the upper plate, and a concentrated solution of copper sulphate is produced above the lower plate. The cell after charging is in reality a gravity primary cell (Callaud cell), which yields a current until all the copper sulphate is transformed into zinc sulphate.

Matche Cell.—Zinc, dilute sulphuric acid, plate of manganese peroxide agglomerated with powdered carbon. When the cell is exhausted it is regenerated by passing a current through it.

Zenger Cell (1885).—Zinc^{Hg}, acidulated water; porous cup, bromine, carbon E. M. F. = 1.95 to 2.2 volts. The bromine is

at the bottom of the porous cup, which is filled with pieces o.' retort-carbon (and closed by a paraffined cover provided with a stopper, for insertion of the liquid bromine) covered with a layer of ferric chloride. The zinc is placed in a 10% solution of hydrochloric acid to which from 5 to 10 per cent of glycerine is added. When the current has become reduced to about ⅓ intensity the cell may be regenerated by a dynamo current in a short time, through the very easy reduction of the bromine.

Dry or Static Electricity Accumulators.—Elster and Geitel have interposed between the conductors of a Holtz machine a dry Zamboni pile of 11,000 elements of 1 sq. cm. section. The copper terminal touches the positive and the tin terminal communicates with the negative conductor of the machine. At the end of 10 minutes the E. M. F. of the pile became sufficiently high to cause a spark between the terminals at 1 mm. distance in air. The authors have also tested a dry accumulator of the Planté type. On each face of a sheet of lead was glued a sheet of silk paper impregnated with a solution of silicate of potash to which a little lead oxide was added. The sheet was cut into small disks of 1 sq. cm., 7000 of which were piled together. When arranged as described above this accumulator gave more powerful effects than did the Zamboni pile.

CHAPTER XXIII.

ACCUMULATORS. (*Continued.*)

V. GENERAL PRACTICAL DATA, TABLES, ETC.

Capacity.—The capacity of an accumulator is the amount of energy it is capable of storing, and is calculated generally in ampere-hours, or the product of the number of amperes at which a cell is able to discharge into the number of hours through which the discharge is maintained. Capacity is also estimated by the ratio between the weight of the material and the electrical output. Thus the ordinary form of cells (applied active material) yields about 4 ampere-hours per pound of plate complete. The amount of surface exposed to the solution really determines the charge which a cell can receive, and is therefore a measure of its capacity. Reynier estimates the capacities of various types of cells per kilogram as follows:

Planté type.........from 2 to 17 ampere-hours.
Lead-copper type.... " 3 " 8 "
Lead-zinc type....... " 3 " 8 "
Alkaline zincate...... " 0 " 41 "

Work.—The utilizable electrical work of an accumulator is expressed in volt-coulombs or joules by the formula $W = Qe$, in which Q is the voltaic capacity in coulombs, and e the mean fall of potential in the external circuit. The quantity Q is equal to the product of the mean intensity of the current C in amperes by the time t in seconds, or $Qe = Cte$. As 1 kilogram-metre = 9.81 joules, 1 horse-power hour = 270,000 kilogram-

metres, the external work of an accumulator may be calculated by the formulæ

$$W = Qe = Cte \text{ joules,}$$
$$= \frac{Qe}{9.81} = \frac{Cte}{9.81} \text{ kilogrammetres,}$$
$$= \frac{Qe}{2647700} = \frac{Cte}{2647700} \text{ horse-power hours.}$$

(Reynier).

Power.—The power of an accumulator expressed in watts or volt-amperes is given by the formula

$$P = eC,$$

in which e is the fall of potential in volts, and C the current strength in amperes. The powers of 1 kilogrammetre per second, 1 horse-power, and 1 kilowatt are respectively equal to 9.81 watts, 736 watts, and 1000 watts; whence

$$P = eC \text{ watts} = \frac{eC}{9.81} \text{ kilogrammetres per second,}$$
$$= \frac{eC}{736} \text{ metric horse-power,}$$
$$= \frac{eC}{746} \text{ English horse-power,}$$
$$= \frac{eC}{1000} \text{ kilowatts.}$$

Efficiency.—This is the ratio of the energy taken out of a cell as compared to that put into it. The former cannot, of course, equal the latter. The efficiency of cells of the ordinary sizes discharged to their proper minimum E. M. F. ranges between 65 and 70 per cent. It depends very largely on the rate at which the energy is discharged—that is, upon the current strength per unit of surface or "current density." The highest safe rate, 4 amperes per positive plate, is equal to 0.001 ampere per square millimetre of surface. The following experi-

ment with a small cell quoted by Mr. W. H. Preece shows how the efficiency varied with the rate of discharge or current density, thus:

Current Density.	Ampere-hours.
0.013	44.6
0.048	30.5
0.090	30.2

It may be stated that the lower the density the greater the efficiency, for with small cells slowly discharged an efficiency or electrical return of upwards of 95 per cent has been obtained. With a cell discharging at the rate of 5 amperes an efficiency of 90 per cent might be obtained, but on increasing the current to 40 amperes the output falls to about 50 per cent; for when the rate of discharge is high the E. M. F. is rapidly reduced.

Charging and Maintenance of Accumulators.—The charging current should be proportional to the number of plates, and is usually about 4 amperes per positive plate. When the current exceeds that amount it cannot increase the reduction of the lead sulphate in proportion to the extra amount of current, and the surplus current is therefore wasted in the decomposition of water and the premature evolution of bubbles of oxygen gas from the positive surface, a phenomenon which is technically known as "boiling." There is also a risk that the two powerful currents will cause bending or buckling of the plates, which, being very close together, stand a good chance of making contact one with the other, and so short-circuiting the cell. Precaution has also to be taken that the electromotive force of the charging current should exceed that of the subsequent discharging current by about 10 per cent, or be at the rate of about 2.5 volts per cell, being, however, a little lower at starting than when approaching the completion of the charge. The charging should be continued until the solution assumes a milky appearance consequent on the evolution of free oxygen, the positive plates having then absorbed as much of the gas as they can take up. The E. M. F. of a secondary cell rises, although not uniformly, with the continuance of the

charging current. In some important experiments, performed by Messrs. Drake and Gorham with a battery of 15 cells, a current of 22 amperes was employed by which the E. M. F. was raised from 2.02 to 2.53 volts per cell. After 220 ampere-hours had been put in, that is to say, after a charging current of 22 amperes had been maintained for a period of 10 hours, the E. M. F. had risen gradually to 2.13 volts. After about 14 hours' charging, when the E. M. F. was 2.17 volts, a somewhat sudden rise in E. M. F. was observed, which was continued until 2.53 volts were registered. The maximum E. M. F. usually obtained is 2.5 volts, at which point gases are freely evolved and cause the milky appearance already referred to as "boiling." It was for some years considered to be very injurious to charge the battery to an E. M. F. exceeding about 2.25 volts per cell, it being thought that charging beyond this point, or overcharging as it was called, was responsible for the remarkable tendency of the plates to buckle or twist out of shape, and so to loosen and detach the pellets.

This, it was supposed, was brought about by the freed oxygen destroying the grid. It has, however, been conclusively proved that overcharging is not only harmless, but actually beneficial. The following practical suggestions are from Slingo and Brooker's " Electrical Engineering."

Solution.—The solution, prior to charging, should be put in the cells to the height of about $\frac{1}{2}$ inch above the negative plates. It should contain about 20 per cent of pure sulphuric acid and have a specific gravity of 1.170 (that is, if a given volume of water weighs, say, one pound, the weight of an equal volume of the solution should be 1.170 pounds).

During the discharge the density of the solution falls until, when the cell is practically exhausted, it is only 1.150. The relative density of the solution thus affords an excellent means of ascertaining the condition of the cell.

Color of the Plates.—The color of the plates affords another good indication of their quality, the peroxidized positive plate being of a brownish or deep reddish hue, and the negative or spongy lead plate being colored gray or slate-tint. There is

thus a marked distinction in the coloration, which should always be discernible.

Discharge.—During the discharge the E. M. F. of the cells speedily falls to about two volts each, the higher initial electromotive force being no doubt mainly due to the presence of hydrogen on the spongy lead plate. When this has been oxidized there remains the lead surface, between which and the peroxide plate the electromotive force falls very slowly to about 1.98 volts. The fall is then slightly faster, although after an output of 400 ampere-hours, at the rate of 25 amperes, the total drop from the time that the cell settles down to steady work at 2.02 volts is only about ten per cent. The rate at which the fall of E. M. F. takes place was clearly shown by the experiments of Messrs. Drake and Gorham, before referred to. The discharge was continued, however, until the E. M. F. was only 1.80 volts per cell, which is a point about 0.1 lower than it is practically advisable to go. With a fall to 1.90 volts the difference is only about 5 per cent.

In an experiment performed to ascertain the effect upon the plates of a rapid discharge, a battery was divided into two halves, one of which (A) was repeatedly run out, but the other (B) was never discharged beyond the point at which the E. M. F. commenced to drop. The experiment extended over a considerable time, but gave the instructive result that, when exactly the same number of ampere-hours had been taken out of each half, the plates of (A) showed signs of expansion or growing, whereas in those of (B) no change could be detected. The life of the grid was therefore proved to be dependent, not on the *amount* of ampere-hours taken out, or on the work done, but on the treatment of the plates.

Buckling.—This appears to be due to the expansion of the paste during sulphating, for lead, being a very ductile but non-elastic body, does not reassume its proper shape when the subsequent partial contraction of the paste takes place; and to this must also be attributed the loosening of the pellets. The contraction being but partial, the positive plates become gradually increased in size with continued use.

Sulphating.—When the rate of discharge is too great there is considerable risk of causing unequal expansion of the plates, resulting sooner or later in buckling, loosening of the pellets, and short-circuiting. It is impossible to prevent a certain amount of the obdurate sulphate forming, and this, being an insulator, reduces the available active surface and increases the resistance of the cell. As already indicated, considerable difficulty is experienced in removing this sulphate, and under any circumstances a certain amount of disintegration of the peroxide is sure to ensue.

But experiments have been performed which tend to show that, with a considerable increase in the charging E. M. F., the sulphate can be decomposed. Its formation can be to some extent prevented by the addition of a small percentage of sodium sulphate (Na_2SO_4).

If the cells are discharged and then left to stand idle for any length of time, the sulphating takes place rapidly and causes premature buckling.

Faults of Lead and Lead Peroxide Accumulators.— Mr. G. H. Robertson (1892) concludes, as the result of experiment with numerous forms of accumulator, that from "the same faults appearing in batteries of such different construction, and judging also from the results of the experiments recorded in this paper, it would appear that the troubles occurring in batteries are due rather to causes arising in the working than in the manufacture. What is required is some substance which can be added to the acid to check the formation of the oxidized bodies in it which cause sulphating, without at the same time injuring the plates in other ways. Nearly all the 'forming' baths which have been introduced are baths in which hydrogen dioxide would be broken up as soon as formed, and, perhaps, in some modification of them the electrolyte of the future will be found; though, since the products of the electrolysis of sulphuric acid vary with the strength of the acid and the current density, no hard and fast rule can be laid down for the treatment of cells.

"In cells containing acid below density 1.200, in which the

proportion of 'active oxygen' existing as hydrogen dioxide is high, the addition of 1 per cent of sodium sulphate, or similar substance, is likely to prove beneficial, particularly if the work of the cells is intermittent. As the strength of the acid is increased, however, and the conditions are more favorable to the stability of persulphuric acid, less hydrogen dioxide will be produced, and there is more chance of the alkali released from the sodium sulphate during electrolysis damaging the plates.

"Also, Dr. Marshall has succeeded in preparing pure persulphuric acid, and has shown that it forms salts with the alkalies which are very stable; and what the effect on a cell of the formation of sodium persulphate in it would be is quite unknown. Although the formation of peroxides in the acid does not apparently account for the great gasing and sudden loss of charge sometimes observed, still we have seen that makers are reverting to Planté's process of manufacture, or modifications of it, and we may find that in this case also he was right, and that it is to the electrolyte we must look if we wish to find the means of materially improving the lead reversible battery."

The Inherent Defects of Lead Storage Batteries.— In a paper on this subject (Proc. Am. Inst. Elec. Engrs. 1889) Dr. L. Duncan and Mr. H. Weigand state the principal defects to be "(1) the comparatively small storage capacity, (2) the loss of energy, (3) the depreciation, (4) the low discharge rate necessitated by considerations of efficiency and depreciation. The question of the loss of energy in the battery was investigated. There are two factors which determine the extent of this loss. In the first place, the number of ampere-hours obtained on the discharge of the cell is less than the number put in; and in the second place, the potential difference at the terminals is greater during charge than during discharge. This loss of energy exhibits itself in two ways —in the generation of heat, and in chemical actions which are not reversed on discharge. It is well known that after a cell has been in use for some time, especially if it be submitted to rapid charge and discharge, there will be found in the bottom of the containing vessel a white powdery deposit, a sulphate of lead

which has been formed from the active material of the plates and which has not been afterwards reversed. Again, when the cell is charged we find bubbles of gas escaping from the plates during almost the whole of the charge, the escape becoming quite violent towards the last. The escape is at first principally from the positive plate, but afterwards it is from both plates. This escape represents, of course, a loss of energy due to the electrolysis of the dilute acid in the cell, the products being free hydrogen and oxygen."

The experiments made by the authors show : " In the first place, the loss that exhibits itself in heating increases as the charge or discharge goes on, not being very great in the latter operation until the potential difference has begun to fall. The loss is greater during charge than during discharge. For instance, take a discharge at 15 amperes : the potential difference begins to fall when 60 ampere-hours have been taken out. The total rise in temperature is 2.03 degrees, while the rise due to the heating of the current alone (C^2R) should be $3°.4$. In other words, there has been an absolute lowering of temperature by all the other actions outside of the Joule effect. Taking a charge at 10 amperes, the rise for a charge of 100 ampere-hours was $8°.9$, with a loss due to the Joule effect corresponding to $3°$, a difference of $5°.9$. The difference in the losses for charge and discharge—neglecting C^2R—is about $5°.3$. For a charge of 120 ampere-hours at 10 amperes the rise was $11°.15$."

" We will find the same results in all of the other records, there being sometimes an absolute fall of temperature on discharge. This is without doubt largely due to the fact that the acid is strengthened on charge, weakened on discharge. In changing from a specific gravity of 1.14 to 1.18, the evolution of heat is such as to raise the temperature of the solution about $3°.2$: there will be a corresponding cooling effect on discharge."

" To the above charge at 10 amperes there was a discharge at 20 amperes, which gave a total of 84 ampere-hours, of which 60 were at normal P. D.; the rise for normal P. D. was $2°.0$; total rise, $4°.7$. $C^2R = 12.1$ for the 60 ampere-hours, corresponding to $3°.8$; the total value of C^2R for the 84 ampere-hours

was 15.1, corresponding to 4°.7. The total heat-loss in the process of charge and discharge was $11.15 + 4.7 = 16°.2$, or about 51 watts. The total loss obtained from taking the difference between charge and discharge energies calculated from the ampere-hours and P. D. was 98 watts, more than half of which appeared as heat. Of the 51 watts which appeared as heat, 27 were due to the Joule effect, 34 to other causes. The authors believe that part of this loss—a very small part—is due to local action betweeen the positive material and the support plate. Another part is due to local currents in the plugs themselves." Another part is due to heat-losses corresponding to electrolysis of solution into free O and H.

" But there are 47 watts left unaccounted for, which must be due to chemical changes not reversed. The most important of these, as far as loss of energy is concerned, is doubtless the formation of free H and O. Another component of the 47 watts is due to the local action between the plugs and support." The authors state in conclusion : " We believe the most important, as far as deterioration is concerned, is in the corrosion of the support and the formation of irreversible compounds caused by the weakening of the acid in the plugs. We have found that the rate of diffusion in the plug is comparatively slow, so that during a rapid discharge there must be weak acid in the plug. Where the outer layer of active material is reduced, the inner layer is surrounded by weak acid, causing a lowering of the E. M. F. and corrosion, as described by Gladstone and Tribe, with a considerable local action between the outer and inner layers. As the rate of diffusion is less with a partly discharged than with a charged plate, a heavy discharge rate has a more marked effect with a partly discharged than with a fresh cell, as experience has shown."   .

" These are, we believe, the principal sources of loss in a lead secondary battery, and the depreciation can be mainly charged to them. The expansion and contraction of the plugs in a grid plate is another source of trouble and cannot be avoided. Our own experience has been that the losses are less with plane plates coated with thin layers of active material

than with plates made of the grid form.   Under any circum-
stances, an increase of surface for a given current rate is to be
desired, as it lengthens the time of charge before the violent
boiling occurs.   A plane plate gives a uniform distribution of
current, and, therefore, very little local action."

Number of Kilogrammetres given per Kilogram by Various Accumulators.

F. Geraldy (1883) has collected the following results :

Accumulator.	Kilogrammetres.
Planté (experiments of Hospitalier & Geraldy)	3450
Faure (old type : experiments of Allard, Joubert, Fresca, and Poitier)	3000
Faure (experiments of Ayrton and Perry)	3500
Schulze (experiments of Hallwachs)	3200
" (" " Aron)	3400
Kabath (" " ")	3400
Faure-Sellon-Volckmar (experiments of Fichet, Hospitalier, Jousselin)	3015 3375 4212
Faure-Sellon-Volckmar (experiments of Monnier & Guitton)	3834

Coefficient of Reduction.—E. Reynier (1884) applies the
term coefficient of reduction (*coefficient de baisse*) to the rela-
tion between the minimum E. M. F. of charge and the maxi-
mum E. M. F. of discharge of an accumulator.   In the Planté
accumulators the E. M. F. is at least 1.95 volts during charge
and at the most 1.85 during discharge.*

The coefficient of reduction is, therefore,

$$\frac{1.85 \text{ volts}}{1.95 \text{ volts}} = 0.95 \text{ volt}$$

under the most favorable conditions.

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* These figures are applicable to all systems of accumulators derived from
the Planté, or, in other words, those which consist of reduced lead, peroxidized
lead, and dilute sulphuric acid.

In copper accumulators the E. M. F. is at least 1.43 volts during charge and at most 1.25 volts during discharge. The coefficient of reduction is, therefore,

$$\frac{1.25 \text{ volts}}{1.43 \text{ volts}} = 0.87 \text{ volt}$$

under the most favorable conditions. The copper accumulator therefore shows the greater loss.

In the amalgamated zinc accumulator the E. M. F. is at least 2.4 volts during charge and at most 2.36 volts during discharge. The coefficient of reduction is, therefore,

$$\frac{2.36 \text{ volts}}{2.40 \text{ volts}} = 0.983 \text{ volt}$$

under the most favorable conditions. The amalgamated zinc accumulator therefore shows the least loss.

Testing Storage Batteries.—The following is the record of a test of three accumulator-cells of similar construction made by Drs. L. Duncan and G. A. Liebig, Jr., at Johns Hopkins University. The type of accumulator experimented upon is not here material, the record being given to show the usual mode of conducting a test of this description. The quantities to be determined were : 1st, capacity; 2d, internal resistance ; 3d, durability ; and 4th, efficiency—the latter as far as possible in widely differing conditions of charge and discharge. The three forms of cell were distinguished by the marks 25 M., 15 M., and 11 P., respectively.

I. *Capacity.* TYPE 25 M. These cells are of twenty-three plates, eleven positive and twelve negative. The weight of the plates as joined up in the cell with lead connections was 84 lbs.

Dec. 20 to 28. Charge, Table I—Mean current, 16 amperes; mean E. M. F., 2.35 volts ; total charge, 420 ampere-hours. Discharge—Mean current, 17.5 amperes ; mean E. M. F., 1.09 volts ; capacity, 409 ampere-hours ; efficiency, 78 per cent.

January 8 to 14. Charge—Mean current, 23.8 amperes; mean E. M. F., 2.27 volts ; total charge, 453.6 ampere-hours. Discharge—Mean current, 18 amperes ; mean E. M. F., 2.5 volts ; capacity, 378.2 ampere-hours ; efficiency, 75 per cent.

TABLE I.—CELL 25 M.

Charge.	Time.	Current.	E. M. F.	Amp.-hours.
	2.45 A.M...............	16	2	—
	5 P.M.................	16	2.1	36
	8.45 A.M...............	16	2.2	—
	5 P.M.	16	2.4	132
	8 A.M.................	16	2.4	—
	5 P.M.................	16	2.45	144
	8.30 A.M...............	18	2.55	—
	2.30 P.M.	18	2.5	108–420

Discharge.

	Time	Current.	E. M. F.	Amp.-hours.
	4 P.M.................	19	2.1	—
	10 A.M............	19	2	342
	10.50 A.M	17	1.95	38
	12.05 P.M	17	1.85	—
	2.15 P.M.............	12	1.7	29–409
	Discharging all night.			

January 17 to 22. Charge, Table II and Fig. 193.—Mean current, 27 amperes ; mean E. M. F., 2.25 volts ; total charge, 431.6 ampere-hours. Discharge—Mean current, 60 amperes ; mean E. M. F., 1.78 volts ; capacity, 352.4 ampere-hours ; efficiency, 64 per cent.

TYPE 15 M. The first charge of this cell was carried very much beyond the necessary limit, in order to reduce a considerable amount of sulphate which was found on the plate; weight, 67 lbs. 6 oz.

Dec. 4 to 8. Charge—Mean current, 20 amperes ; total charge, 390 ampere-hours. Discharge—Mean current, 19.5 amperes ; mean E. M. F., 2.5 volts ; capacity, 170 ampere-hours ; efficiency, 65 per cent.

TABLE II.—CELL 25 M.

Charge.	Time.	Current.	E. M. F.	Amp.-hours.
	12.15 P.M	28	2	—
	2 P.M	23	2.1	—
	4 P.M	22	2.1	66.9
	10.15 A.M	30	2.15	—
	12 M	28	2.22	—
	5 P.M.	28	2.25	189.5
	11 A.M..	33	2.35	—
	2 P.M.................	27.5	2.5	—
	5 P.M.	27.5	2.5	—
	5 P.M	27.5	2.6	172.2–431.6

Discharge.				
	10.40 A.M	56	1.98	—
	3 P.M................	54	1.85	—
	4 P.M................	26	1.6	322.5
	9.10 A.M.	58	1.95	—
	9.45 A.M.	38	1.60	29.9–352.4

Dec. 26 to 28. Charge, Table III—Mean current, 18 amperes; mean E. M. F., 2.35 volts; total, 255 ampere-hours. Discharge—Mean current, 10 amperes; mean E. M. F., 2.8; capacity, 207.5 ampere-hours; efficiency, 76 per cent.

Jan. 2 to 7. Charge—Mean current, 13 amperes; mean E. M. F., 2.33 volts; total, 279 ampere-hours. Discharge—Mean current, 40 amperes; mean E. M. F., 1.95 volts; capacity, 157 ampere-hours.

TABLE III.—CELL 15 M.

Charge.	Time.	Current.	E. M. F.	Amp.-hours.
	9.30 A.M.	17	2.1	—
	2.15 P.M.............	17	2.1	81
	8.45 A.M. .... ,...	17	2.2	—
	4.15 P.M............. ,.	19	2.3	142.25
	8 A.M................	20	2.45	—
	10.30 A.M	10	2.55	32–255.25

Discharge.

3.55 P.M.	10	2.1	—
10 A.M.	10	1.98	160
10.30 A.M	15	1.95	—
12.30 P.M	10	1.85	—
2 P.M.	10	1.6	47.5–207.5

Discharging during the entire night.

Jan. 8 to 14. Charge, Table IV—Mean current, 14 amperes; mean E. M. F., 2.35 volts; total charge, 238.8 ampere-hours. Discharge—Mean current, 15 amperes; mean E. M. F., 2.6 volts; capacity, 216 ampere-hours; efficiency, 83 per cent.

Jan. 21. Charge—Mean current, 25 amperes; mean E.M.F., 1.6 volts; total charge, 250.2 ampere-hours. Discharge—Short circuit, mean current, 250 amperes; capacity, 83 ampere-hours. This cell was charged and discharged at very high rates: charging rates, 75 to 85 amperes; discharge rates, 250 amperes. This was done repeatedly.

TABLE IV.—CELL 15 M.

Charge.	Time.	Current.	E. M. F.	Amp hours.
	10.45 A.M	13	2.15	78.6
	2 P.M.	12.5	2.15	—
	5 P.M.	12	2.15	—
	10.15 A.M	12.5	2.23	—
	3.30 P.M.	16.5	2.45	83.2
	11 A.M.	16	2.45	—
	4 P.M.	15	2.55	77–238.8
Discharge.				
	9.40 A.M.	15	2.18	—
	2.15 P.M.	15	2	—
	4.20 P.M.	15	2	100
	9 A.M.	15	2.15	—
	1.30 P.M.	14.5	2	—
	4 P.M.	13.8	2	102.6
	9 P.M.	14	2.05	—
	10.30 P.M	4	1	13.5–216.1

TYPE II P. Weight of plate and connections, 23 lbs. 5 oz.
Dec. 12 to 17. Charge, Table V—Mean current, 84 am-
peres ; mean E. M. F., 2.21 volts; total charge, 112.65 ampere-
hours. Discharge—Mean current, 9.6 amperes ; mean E.M.F.,
1.95 volts; capacity, 95.9 ampere-hours ; efficiency, 75 per cent.

TABLE V.—CELL II P.

Charge. Time.	Current.	E. M. F.	Amp.-hours.
9 A.M.	10	2.1	—
5 P.M.	9.5	2.25	78
9 A.M.	6.6	2.35	—
12 M.	9.5	2.5	28.65
12.40 P.M.	9	2.55	6–112.65
Discharge.			
11 A.M.	9.5	2.05	—
2 P.M.	9.7	1.95	—
4.20 P.M.	9.6	1.85	51.2
10.20 A.M	10	2.05	—
2.10 P.M.	9	1.95	—
3.20 A.M.	7.3	1.6	44.7–95.9

The accompanying diagrams, Figs. 191 to 196, exhibit gra-
phically the operation of the cells during the tests.
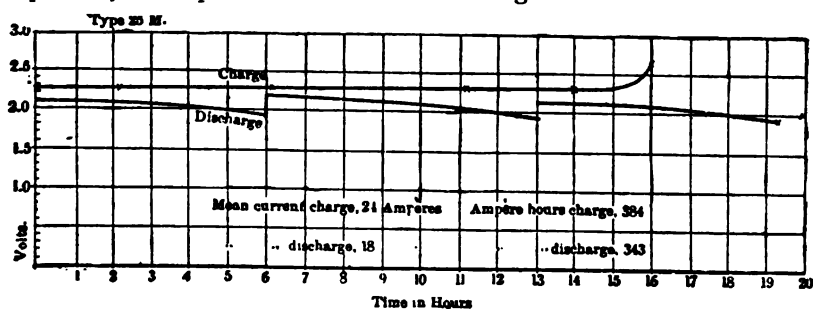
FIG. 191.

II. *Internal Resistance.* TYPE 25 M.—For mean current,
.0036 ohm.
TYPE 15 M.—For mean current, .0064 ohm.
TYPE II P.—For mean current, .0085 ohm.

III. *Durability.* As far as can be seen, the cells are in excellent condition, and no signs of deterioration are as yet
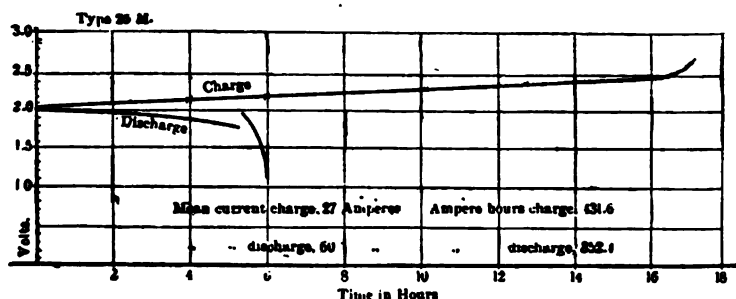
Fig. 192.
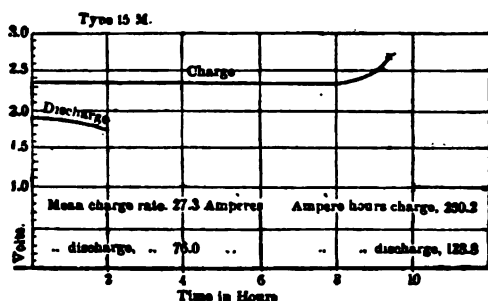
Fig. 193.
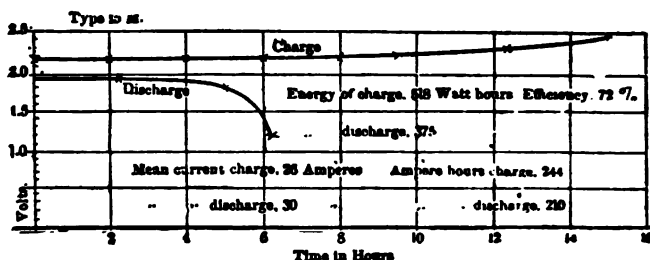
Fig. 194.

evident. The cell 15 M, whose normal discharge rate is 20–25 amperes, was short-circuited a number of times through about four feet of No. 8 copper wire, its resistance being about .0028

·ohm. (**Fig. 196.**) The discharge rate in the cell was very high, being more than 250 amperes ; the cell, however, seems to have suffered nothing by the treatment. The plates have not "buckled," nor have we found parts of the active material forced out from the pores."
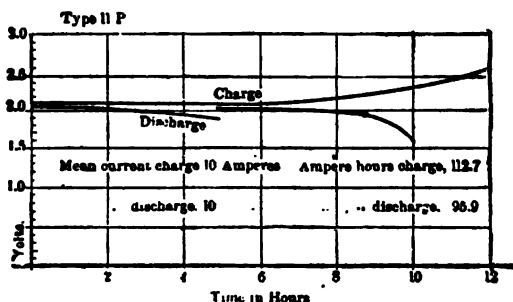
FIG. 195.
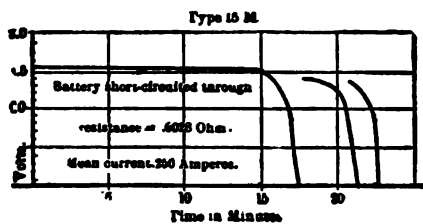
FIG. 196.

IV. *Efficiency.*—" The values of the efficiency vary with the rate of charge and discharge. For the normal rates of discharge the efficiency of the different types of cell examined is between 75 and 80 per cent. In some cases the values are low ; this is due to the cell having been previously run down below the ordinary limit."

Calculating Storage-battery Plants.

The following diagram (Fig. 197) gives a convenient short cut to computing the number of accumulators necessary to run any given number of incandescent lamps. It has been devised by the Consolidated Electric Storage Company with

special reference to a standard type of cell (S 17), which has a nominal capacity of 180 ampere-hours at a 10-ampere discharge rate. Its maximum rate of charge is 15 amperes; its maxi-
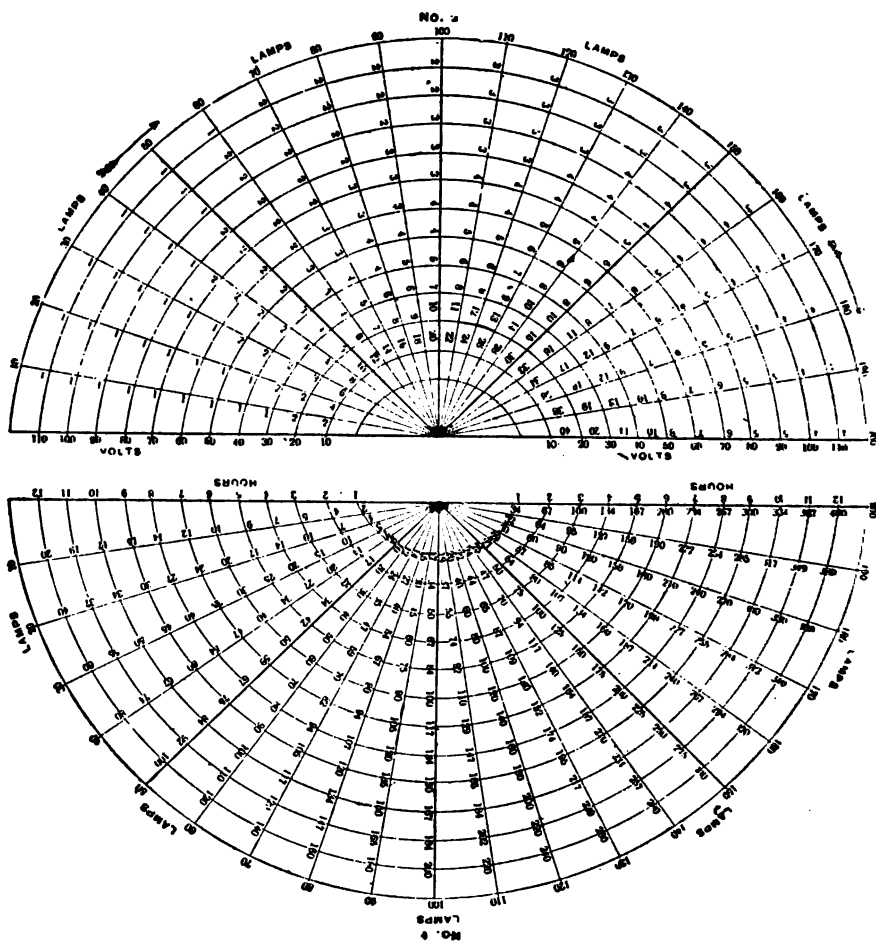
FIG. 197.

mum rate of discharge, 20 amperes. It occupies floor-space 7 × 8 inches, is 10 inches high, and weighs, complete, 42 pounds in a glass jar or 35 pounds in a lighter rubber jar.

The tables give a rough approximation to the number of accumulators required, whatever the make, provided the type is equivalent to the one just described. The upper half of the diagram enables one to tell at a glance the number of accumulators required to operate any number of lamps up to 200 any number of hours from one to twelve. For example: Suppose we want to run 120 lamps nine hours per night. Glance along the list of hours and follow the circle marked "9" around until it cuts the radius corresponding to the number of lamps; we see that 180 accumulators are required. But how shall they be arranged? This evidently depends on the voltage of the lamp. A 55-volt lamp would require only half as many accumulators in series as a 110-volt lamp. The lower half of the diagram, No. 2, gives an instantaneous means for ascertaining this. It shows the number of series which must be placed in parallel to make up the total number of accumulators. For example: Suppose the 120 lamps just mentioned were to be 110-volt lamps. Follow the voltage circle corresponding to 110 around until it cuts the radius corresponding to 120 lamps, and we find figure 3. This means that we are to have three series of accumulators in parallel, and since 180 cells were required in all we shall have 60 accumulators in series, and three such series coupled in parallel.

It should be understood that in case No. 2 of the diagram should give a number of series which does not contain the integral a number of times in the total number of accumulators, euough should be added to fill the requisite number of series up to the even amount. In other words, if there should be a remainder on dividing, enough accumulators should be added to bring this remainder up to the same amount as the other series.

Indicator for Accumulators.—One of the indications by which the condition of the secondary cell can be determined is that of the density or specific gravity of the electrolyte, which varies with the charge of the cell. An ingenious apparatus has been devised for this purpose by Mr. J. S. Sellon, by which the condition of the cell is shown at all times.

Figs. 198 and 199 show the apparatus in section and in elevation. *A* is a platinum or glass bulb or float which is in the cell. Attached to this is a fine wire of glass or of platinum, to which is joined a silk thread. This silk thread passes over
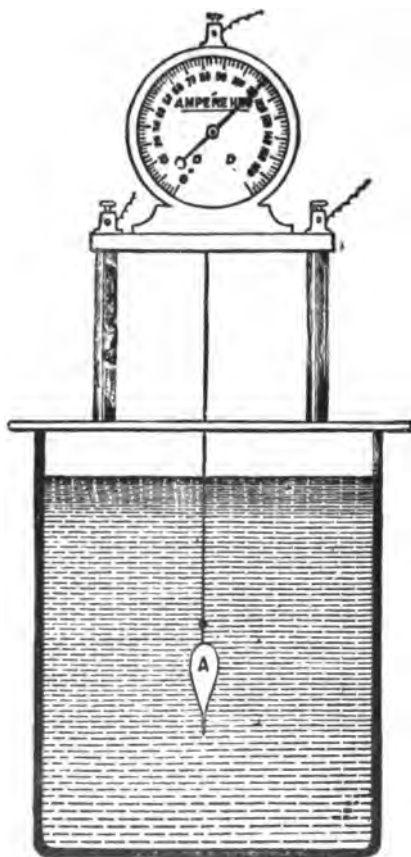
FIG. 198.   INDICATOR FOR ACCUMULATORS.   FIG. 199.

wheel *B*, ending with a cup, *C*, adjusted to the desired weight. This arrangement is similar to the action of a wheel barometer.

Under ordinary conditions of working, 10 degrees of density may be taken as representing 100 ampere-hours, which gives considerable motion to the bulb or float. It is obvious

that the wheel B can be made of such a size as to give large or small readings.

Fig. 200 shows an automatic current manipulator or charging switch, whereby any number of sets of cells may be brought in or cut out of the charging circuit, through the rise and fall
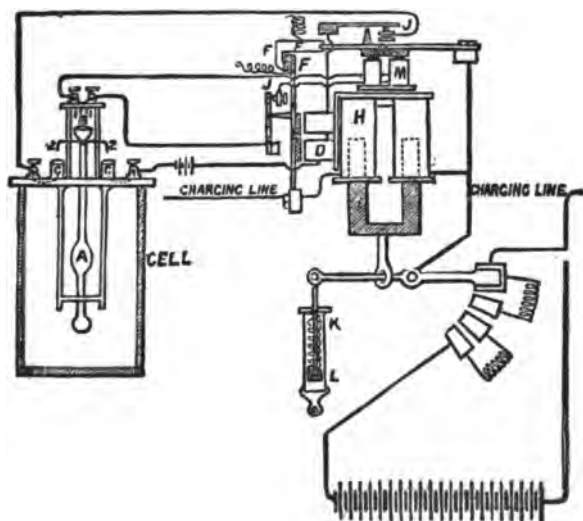
FIG. 200.—INDICATOR FOR ACCUMULATORS.

of the density of the electrolyte. A is an acidometer hydrometer, the motion up and down of which causes wires 1 and 2 to make contact with the mercury in cups B and CC. On the fall of the acidometer through the discharge of the cell, contact is made by wire 2 2 with mercury cups CC; this connects up one or two cells with magnet D. This magnet, by attracting its keeper, E, opens the circuit at FFF; this causes the charging current, if acting, to pass through the wire of solenoid H, which, by attracting its core, I, switches in resistance, short-circuits the same, and finally connects up the cells with the charging main. Contact springs, JJ, break the connection of magnets D and M, opening the one which has operated, closing the other ready for the next operation. This prevents waste of current which would take place, as the contacts at 1

and B and 2 and C remain closed until an alteration of the specific gravity occurs.

The opposite action takes place on completion of charging contacts being made at wires 1 1 with mercury cup B. This actuates magnet M, which, by attracting its keeper, N, causes the end of the keeper E to spring in and lock at FFF, thereby short-circuiting solenoid H, which releases its core, I, spring K in dash-pot L, switching in resistance, connecting up, and thereby disconnecting the set of cells from the charging main.

By this arrangement sets of accumulators can be readily switched in and out of the charging circuit at any desired point of charge or discharge.

WEIGHTS OF CELLS RESPECTIVELY CORRESPONDING TO THE POWER OF 1 H. P. AND TO THE WORK OF 1 HORSE-POWER HOUR. (REYNIER.)

Type of Cell.	Weight corresponding to the power of 1 horse-power. kilograms.	Weight corresponding to the work of 1 horse-power. kilograms.
Planté spiral pattern, very well formed............	200	180
Voltameter regulator, Planté pattern, Ville de Paris model......	110	180
Reynier light plate pattern.........	208	63
Denis Monnier lighting...........	525	85
Faure, 1881.....................	540	108
Faure-Sellon-Volckmar lighting.....	408	62
"　　"　　"　　tramcar....	260	43
Faure-Sellon-Volckmar experimental.....................	200	25.5
Fitzgerald......................	200	31.5
Reynier lead zinc.................	163	80
C. D. B. potash zincate (laboratory experiment)..................	204	23.8
C. D. B. potash zincate (individual experiment).................	170	37

WEIGHT PER HORSE-POWER HOUR CAPACITY OF VARIOUS SECONDARY CELLS.

Name of Cell.	Elements only.		Cell complete.		Authority.
	Lbs.	Kilos.	Lbs.	Kilos.	
Planté	—	—	396	180	Reynier
Faure...... .... }	—	—	88	40	Faure
			165	75	Sir W. Thomson
" (old model)........	—	—	198	90	} Reynier
" (new model).......	—	—	134	61	
E. P. S. L plates...... }	—	—	133	60.4	Prospectus
	—	—	110	50	Reckenzaun
" S " ..... }	66	30	135	61.3	Fitzgerald
Reynier { Zinc, pos.....	50.6	23	117.5	53.4	R. Tamine
{ Planté form...	105	47.6	—	—	"
Lithanode (old form)....	42	19.1	76	34.5	Fitzgerald
" ("Union" cell)	42	19	70	31.5	G. Forbes

STORAGE CAPACITY OF VARIOUS SECONDARY CELLS.

Name of Cell.	Per Pound of Pb.		Per Kilo of Pb.		Authority.
	Foot-pounds.	Watt-houts.	Kilogram-metres.	Watt-hours.	
Planté.................	12,000	4.52	3,664	10	
Faure..................	18,000	6.78	5,495	15	
E. P. S. L plates........	48,000 (?)	18.09(?)	14,600 (?)	39.8 (?)	Howard
" R "	36,080	13..6	11,010	—	Hospitalier
E. P. S. S, nominal 22-lb. cell....	31,800	12	9,540	26	Fitzgerald
Elwell-Parker (old form).	6,633	2.5	2,018	5.5	Prospectus
Lithanode battery (old form)................	39,728	15	12,110	33	Fitzgerald
Lithanode battery ("Union" cell)...............	47,170	17.8	14,671	39.16	G. Forbes

TABLE OF DATA OF SECONDARY BATTERIES. (ROBERTSON.)

Accumulator	Type	Material of Cell: Lead Plates and H_2SO_4 or otherwise.	Capacity in ampere-hours.	Capacity in watt-hours.	Charging Current.	Max. Dis-charging Current.	No. of Plates +	No. of Plates −	Thickness of Plates in inches +	Thickness of Plates in inches −	Total Area of Plates (sq. ft.).
Reynier	......	Lead and lead peroxide in sulphuric acid	30	740	......	6 am.	......	......	......	......	......
B.P.S.	1888 L / 1890 K	Lead grids pasted H_2SO_4 ribbed lead plates pasted; H_2SO_4	130	847	10 to 13 / 15 to 25	13 / 25	3 / 3	4 / 4	......	......	......
Oerlikon	B / E / F / D	Hard lead grid plates made of red lead and litharge. Pasted positives; lead negatives dilute; H_2SO_4	50 / 266 / 166 / 70	95 / 494 / 394 / 133	6 / 30 / 18 / 9	10 / 48 / 25 / 9	4 / 5 / 5 / 8	5 / 6 / 6 / 9	0.2 / 0.2 / 0.2 / 0.1	0.2 / 0.2 / 0.2 / 0.1	1.9 / 8.9 / 5.6 / 3.8
"D.P."	A	Pasted positives; lead negatives dilute; H_2SO_4	140	266	12	12	......	......	......	......	......
Tommasi mul-titubular	H	Red lead and litharge in porous pots; dilute sulphuric acid	775 / 321	1,377 / 642	66 / 25 to 100 amperes	66 / 18 to 30	...... tubes	...... Tian-Rules	0.75 by 2 by 4	9¼ by 2 by 4	......
Julien	S. 17	Pasted plates. Dilute sulphuric acid	180 / 180	......	15 / 15	20 / 20	8 / 8	9 / 9	┿ ┿	┿ ┿	5.4 / 5.4
Gadot	1 A / 10 E	Double grid containing pastilles made from oxides of lead; H_2SO_4	28 / 1063	53.2 / 2,019.7	3.1 amp. / 116	52 / 193	2 / 11	3 / 12	......	......	......
Crompton-Howell	No. 11 / 17 / 21 / 31 / 61	Lead plates and H_2SO_4	220 / 340 / 420 / 620 / 1200	440 / 680 / 840 / 1,200 / 2,440	28 / 42 / 52 / 78 / 152	85 / 135 / 170 / 250 / 500	5 / 10 / 15 / 30 / 10	6 / 9 / 11 / 16 / 31 / 10	┿ ┿ ┿ ┿	┿ ┿ ┿ ┿	11 / 17 / 21 / 31
Atlas	No. 1	Block composed of plates made of oxides and salts of lead; H_2SO_4	150	$\left(\dfrac{2+1.8}{2}\right)$ 285	8	16; normal 10	10	10	0.4	0.4	......
Roberts	Modified Faure twin plate	Lead alloy, H_2SO_4 combined with an alkaline solution	75 / 150 / 250 / 450	162 / 325 / 545 / 990	15 / 25 / 35 / 50	Practically unlimited	2 / 4 / 4 / 8	3 / 5 / 5 / 9	┿	┿	18.8 / 33 / 63 / 108
Legay	......	Plates made of lead wire rope; formed by Planté's process	194	364	20 amperes	200 amperes	4	5	┿	┿	75
Tudor	VII—λ / D	Lead. Lead peroxide in dilute sulphuric acid	240 / 168	456 / 321	18 / 48	24 / 60	......	......	1.3 / 1.3	1.3 / 1.3	......

TABLE OF DATA OF SECONDARY CELLS.—(*Continued.*)

Accumulator.	Amperes per sq. ft. Total Plate Area. Discharge.	Length. (in.)	Br'dth. (in.)	Height. (in.)	Height overall. (in.)	Total Weight of Cell (lbs.).	Ampere-hours per lb. of total weight.	Watt-hours per lb. of total weight.	Efficiency (watt). Per cent.	By whom Efficiency Test was made.
Reynier....	....	12	12	..	12	100	0.3	7.4	....	....
E.P.S.: 1888 L	....	5¼	13⅜	18¼	20¼	74	1.7	3.3	....	....
1980 K	.	5¼	11¼	13¼	16¼	81	....	....	....	....
Oerlikon: B	5	7.8	9.2	8.77	....	39.6	1.25	2.4	....	⎧ Prof. Kohlrausch, Hanover
E	5.4	9	14.4	16.4	....	156.2	1.6	3.1	....	⎨ Dr. Coppe,
F	4.4	9.2	11.7	12.5	....	96.8	1.6	3.1	....	⎩ Zurich
D	2.3	5.5	6.8	8.6	....	26.4	2.6	5.0	....	....
"D. P.": A	....	13¼	8	12¼	....	65	2.1	4	....	....
H. Tommasi Multitubular	....	13¾	18	12¼	....	240 Total weight of electrodes 47.7	Per lb. of electrode 6.7	5.7	80	....
Julien S. 17 ⎰	3.6	8	7	10	....	42	4.3		....	....
⎱	3.6	7¼	5¼	9	....	37¼	4.8		....	....
Gadot: 1 A	....	7	3½	....	13.6	17.6	1.6	3	....	....
10 E	....	21.6	20.4	....	20¼	792	1.4	2.66	....	....
Crompton Howell: No. 11	10 at 10	8¼	12¼	12	14	115	1.9	3.8	85; current efficiency 93 to 95	Kennedy Crompton, engineer, of Kensington and Knight's Bridge Company
17		13¼	12¼	12	14	182	1.9	3.8		
21	10 at 3	16¼	12¼	12	14	220	1.9	3.8		
31		29	12¼	12	14	460	1.4	2.8		
61	20 at 6	54¼	12¼	12	14	880	1.4	2.8		
Atlas No 1....	....	7	6.29	12.57	13.75	Plates, 17.63; acid, 6.6; vessel, 2.2 to 8.8	9.6 per lb. of plates, 5.4 to 7 per lb. of total weight	16.1 per lb. of plates; 8.6 to 10.9 per lb. of total weight	....	....
Roberts modified Faure twin plate	4	7¼	2¾	10	12	20	3.75	8.01	87 to 93, according to rate of discharge	G.M.S. Wilton, sec. Acc. Co. Toronto; Wm. Roberts, Elec. Acc. Co, Toronto
	4	7½	5	10	12	38	3.95	8.55		
	4	9¼	5	12	13¼	70	3.55	7.71		
	4	9¼	10	12	13¼	110	4.09	9.00		
Legay ...	4 (about)	9	9	9	11¼	65; plates, 44.1	3.07	5.6	....	Laboratory of Société Internationale des Electriciens
Tudor VII A	....	....	....	....	....	112.2	2.1	....	....	....
D	....	....	....	....	....	112.2	1.5	....	....	....

TABLE SHOWING RELATIVE MERITS OF ACCUMULATORS. (TAMINE.)

	Lead Accumulator.		Copper Accumulator.	Zinc Accumulator.
	Natural Deposit.	Artificial Deposit (Agglomerated Elements).		
Polarization..........	Very perceptible	Perceptible	Scarcely perceptible	Scarcely perceptible
E. M. F...............	1.9 volts after 1000 hours formation	2.15 volts after 1 hour formation	1.26 volts	2.36 volts
Resistance...........	0.005 ohm minimum	0.005 ohm minimum	0.04 ohm minimum	0.04 ohm minimum
Chemical equation of discharge	*Principal Action :* $Pb + H_2O + PbO_2 =$ $PbO + H_2O + PbO$ *Secondary Action :* $PbO + SO_4H_2 =$ $SO_4Pb + H_2O$	*Principal Action :* $Pb + H_2O + PbO_2 =$ $PbO + H_2O + PbO$ *Secondary Action :* $PbO + SO_4H_2 =$ $SO_4Pb + H_2O$	$Cu Cu + SO_4H_2 + PbO_2 =$ $Cu + SO_4Cu + H_2O + PbO$	$ZnZn + SO_4H_2 + PbO_2 =$ $Zn + SO_4Zn + H_2O + PbO$
Formation...........	Very slow	Very rapid	Very rapid	Very rapid
Charge	From 0.25 to 1 ampere per kg. of electrode	From 0.25 to 1 amp. per kg. of electrode	From 0.25 to 1 ampere per kg. of electrode	From 0.25 to 1 amp. per kg. of electrode
Conservation of charge	Months	Months	Loss very perceptible after 15 days	All gone after a few days
Discharge............	1 amp. max. per kg.	1 amp. max. per kg.	2 amp. max per kg.	3 amp. maximum per kg.
Yield................	78.9 per cent	78.9 per cent	72 per cent	Local action prevents practical determination
Weight of electrode necessary per horse-power hour........	11.5 kg.	11.5 kg.	13.3 kg.	7.2 kg.

CHAPTER XXIV.

VARIOUS SOURCES OF ELECTRICITY.

Production of Electricity by Pressure.—Certain mineral substances possess the property of becoming electric to a simple pressure between the fingers. Hauy (1816) placed the bodies upon which he wished to experiment on a piece of marble, with their rubbed faces underneath. He took them, from time to time, with his fingers or with a pincers, and presented them to the needle of his apparatus. He obtained the following results:

The cut topaz of the clear, Brazilian variety conserved its electricity for 32 hours. The electric state of hyaline corundum, emerald, spinel, and other stones used as gems lasted from 5 to 6 hours, but terminated in the cases of diamond and rock crystal after 15 or 20 minutes. Colored glass has very little power for retaining its electric condition. The pressure of a metallic disk against a piece of taffeta coated with elastic resin develops electricity; the disk becoming negatively charged. If, however, the disk is also rubbed while under pressure, it takes positive electricity (Libes).

Quartz also possesses this property, and the three binary, horizontal axes are the directions in which the electric manifestations are maxima. If a crystal be compressed in the direction of one of its horizontal axes, the side on which the hemihedral faces are found becomes positively charged by pressure and negatively by traction. The direction of the disengagement of the electricity is independent of the direction of rotatory power. The quantity of electricity produced

by quartz under a pressure of 1 kg. exerted in the direction of a binary axis is equal to 0.068 C. G. S. electrostatic units. It is capable of raising a sphere of 16.8 cm. diameter to the potential of a Daniell couple.

Zasareff's Pressure Cell.—The production of electricity in this cell is due to the passage of a glycerine solution under pressure through a mixture of coke and anthracite.

Electricity produced by Vibrations.—By vibrating a wire formed of two consecutive parts, one of brass and the other of iron, a feeble current is obtained, according to Sullivan, which ceases with vibration. With a bar of antimony soldered to a bar of bismuth the effect is much more pronounced. It suffices simply to set the bar in vibration and to strike it with a piece of iron. A current is also obtained by vibrating a bar of iron of which one portion is hard and crystallized and the other soft and fibrous. If an ordinary tuning-fork or any body emitting sonorous vibrations be placed in contact with a thermopile connected to a very sensitive galvanometer, the needle will be deflected (Dolbear, 1874).

Electrostatic Polarity by Vibrations (Volpicelli.)—When rods of glass, gum-lac, or sulphur are slid to and fro in one or more metal rings, insulated or not, it is found that the rods present at their ends contrary electricities separated by a neutral line. The extremity thus in advance during the sliding is positive with glass or negative with the resins or sulphur.

Electric Currents obtained by the Bending of Metals (Volpicelli, 1872).—The least flexure produced in an elongated piece of metal produces an electric current when the metal forms part of a closed conducting circuit. This current is obtained with all metals, even with those totally inelastic; such, for example, as lead. Of the metals examined, copper gives the strongest current. If the bending be done by separating one from the other the two ends of the elongated piece of metal, a current is obtained in the opposite direction to that which is manifested when the same ends are brought together. These currents, while opposite in direction, are equal in intensity. Volpicelli calls the first "current of opening," and the

second "current of closing." Equal elongated pieces of metal superposed one on the other produce a flexure current less intense than that which is yielded by a single piece of metal. Other things being equal, by increasing the number of folds in the elongated piece the intensity of the flexure current is diminished, so that maximum intensity is obtained when there are no folds. An elongated piece formed of different metals soldered together, other things being equal, produces a flexure current less intense than that which is yielded by the same length formed of a single metal. By connecting together the terminals of a galvanometer, no matter how short they may be, and then subjecting them to the least flexure, a perceptible deviation of the needle is obtained. It follows, therefore, in using such instruments, especially delicate ones, that the terminals should not be subjected to any bending.

Electricity produced by Cleavage.—When a body which is a bad conductor of electricity, such as mica, is cloven, it is found that each of the separate faces possesses an excess of contrary electricity, the intensity of which is greater in proportion to the rapidity of separation. When a crystal which is a conductor of electricity, such as galena or pyrites, is cloven, no sign of electricity is manifest.

Electricity produced by Destruction of Molecular Attraction between two Heterogeneous Substances.—If fused sulphur be poured into a conical glass previously warmed, and if there be immersed therein, before cooling, a glass tube for the purpose of drawing the sulphur from the glass receiver, it is found that when the cone of sulphur is withdrawn after solidification, the glass possesses an excess of negative, and the sulphur an excess of positive, electricity. Mercurous chloride, sublimated and condensed in the neck of a glass retort, also becomes electrified when mechanically separated (Wilke).

Electricity produced by the Friction of a Solid and a Liquid.—All inoxidizable bodies become negatively electrified on movement, whether they be in contact with distilled water or other more conducting liquids. If powdered carbon be mixed

with the water, the plate which is moved takes positive elec-
tricity (E. Becquerel).

**Electricity produced by the Friction of certain badly-
conducting Bodies against Mercury.**—According to Bec-
querel, electricity may be produced by friction against mercury
by plunging therein, while dry, bodies either suddenly or
slowly, or even by immersing them in mercury and allowing
them to remain there for some time. The production of elec-
tricity takes place between certain limits of temperature which
vary for every body. Thus, amber begins to become electric
from 11° C.; Spanish wax from 15°; glass from 20°; the
temperature of the mercury being the same as that of the
introduced bodies. A high temperature, like a low one,
prevents bodies from becoming electrolyzed by friction against
mercury and the bodies immersed therein. The latter be-
comes electric. There are, however, exceptions to this. Thus,
glass heated to 100° is not electric when plunged in mercury
at 15°; and the same is true on operating inversely.

Paper, wool, cotton, etc., are very electric from 10° up to
80°, even to equality of temperature with the mercury.

Buff (1860) has found that writing-paper, white and flexible,
becomes negative by friction with zinc and copper, and ren-
ders the surface of the metal positive. With platinum it
becomes positive, and the platinum is charged with negative
electricity.

**Electricity produced by the Motion of Liquids through
Capillary Spaces** (Quincke, 1859).—As soon as the flow be-
gins, an electric current is generated, the direction of which
is the same as that of the liquid which traverses the porous
medium, and which ceases when the liquid level is re-estab-
lished. At the moment that the water ceases to pass, an
instantaneous and opposite current is produced due to the
polarization of the electrodes. The effects are the same when
fresh-baked clay, silk, canvas, ivory, etc., are substituted.

By adding to the water a small quantity of acid or alkali,
or of a saline solution, the current diminishes and ends by
almost disappearing. On the other hand, the addition of

alcohol or soap increases the intensity. The direction of the current is independent of the nature of the liquid employed.

The quantity of water transported and the intensity of the current are proportional to the pressure which produced the flow of water.

Neither the thickness nor the section of the porous medium changes the magnitude of the electromotive force.

With distilled water the E. M. F. is about 0.3 volt for a pressure of one atmosphere.

Quincke has found it advantageous to replace the porous earth with a diaphragm of flowers of sulphur; under which conditions a current may be recognized even when very weak pressures are employed.

The following table shows the values determined for the E. M. F.'s, that of the Daniell element being taken as 100.

Substances.	E. M. F.'s.
Sulphur	977
Quartz sand	620
Gum lac	330
Silk	11.5
Terra cotta	36
Asbestos	22
Porcelain	20
Ivory	3
Animal membrane	1.5

The E. M. F.'s which are obtained with sulphur and sand are, as apparent, very considerable; but the low intensity of the currents observed is due to the high resistance of distilled water.

Electricity produced by the Flow of Liquids under High Pressure in Capillary Tubes (Krouchkoll, 1885).—When a conducting liquid is driven through a metallic capillary tube under a pressure below 15 atmospheres, no production of electricity is observed; but when the pressure is increased, the production of electricity becomes perceptible.

With platinum under pressures varying from zero to 200 atmospheres, an E. M. F. of from zero to 0.06 volt is observed.

With copper, an E. M. F. from 0 to 0.063 volt has been noted under pressures included between zero and 250 atmospheres.

The E. M. F. produced under these conditions between the tube and the plate is analogous to the E. M. F. of polarization. It does not appear when a solution of the salt of the metal which forms the tube is driven through the latter. Thus, a solution of copper sulphate produces no effect in a copper tube, whatever may be the pressure under which the liquid flows. The same is true of a solution of zinc sulphate traversing a zinc tube.

Development of Electricity in the Filtration of Mercury (J. Dechant, 1884).—Pfaundler's apparatus consists of an iron tube 45 cm. in length, provided at its upper surface with a glass funnel, and closed at its lower end with a piece of chamois skin which serves as the filtering medium. When mercury is driven through the chamois, it becomes positively electrified. By using different skins of more or less porosity, Dechant has observed that the quantities of electricity developed increase with the fineness of the skin.

Production of Electricity based on Capillarity.—The below-described apparatus, devised by Debrun (1880), is based on the following principle, discovered by Lippmann :

If, by mechanical means, the surface of mercury is deformed, a production of electricity is caused which tends to stop the movement of the mercury.

Mercury is made to flow through a capillary tube, drop by drop, and a supply of acidulated water is arranged so that the liquid is interposed between each globule of mercury. The mercury drops which form the first and last of the series are connected with platinum wires to serve as terminals. The tube is 2.5 mm. in diameter at its upper portion and 1 mm. in diameter at its lower portion. It is 30 cm. in length and contains not less than 20 or more than 35 mercury globules. E M. F.. equals 1.4 volts.

Production of Electricity by Water-jets.—Elster has observed that if a jet of water is .directed against a non-conducting body, the resulting friction may develop an E. M. F. like that which is produced by the flow of water or other liquids through capillary tubes.

According to Edlund, an electric current is also obtainable through the friction of two water-jets upon one another.

Production of Electricity by Watery Vapor or Steam. —W. Patterson (1840) observed that when the finger was gently approached to the lever of a steam-valve while the jet of steam was directed against the other ·hand, a spark appeared between the finger and the lever. This occurred whenever the finger was brought near any part of the boiler, so long as the escaping steam therefrom met some portion of the body.

Armstrong's machine (1841), which is based on this principle, consists of an insulated boiler having a stuffing-box filled with packing wet with cold water, on which are fixed cylinders of box-wood from which the steam escapes. The electricity is collected by presenting to the steam-jet a metal comb supported on a glass column.

The steam pressure used is from 8 to 10 atmospheres, and the electricity seems to be due to the friction of the water-drops, inasmuch as dry steam gives no current. Neither is there any production of electricity unless the water is pure ; the presence of a small quantity of salt or acid being an obstacle. The steam is charged with positive electricity, while the boiler is negatively electrified. If turpentine be added to the water, inverse electric effects are obtained ; that is to say, the steam is negative.

Production of Electricity by Friction of Carbonic Acid. —In producing carbonic acid in the form of snow, according to the experiment of Cailletet, Ducretet has ·found that if a new apparatus made of ebonite be used, the particles of carbonic acid striking against its sides disengage a quantity of electricity sufficient to produce a continued jet of sparks more than 1 cm. in length, which pass between the metallic mount-

ing tube and the nozzle fixed on the receiver containing the carbonic acid.

Production of Electricity by Friction of Air.—A current of moist air, under certain pressure, produces electricity by its friction against the sides of a tube. This is not true of dry air. When dry powders are mixed with the air, there is also a production of electricity, the nature of which depends upon the character of the powders (Faraday).

When air is allowed to escape from a receiver in which it has been compressed, the latter is electrified negatively; in certain cases, however, it may also become positively electrified. With perfectly dry air, there is no production of electricity (Armstrong).

Current produced by the Movement of a Metal in a Liquid (Krouchkoll, 1883).—The current produced by immersion is in opposite direction to that which produces the movement; the current of emersion is in the same direction as the current of movement.

Thus, when a platinum wire, thoroughly depolarized, is plunged in acidulated water, the wire becomes electrified positively at the moment of immersion; it becomes negative during its movement in the liquid, and again becomes negative at the instant when it is withdrawn from the liquid.

The same platinum wire is electrified negatively at the instant when it is plunged into water containing a solution of sodium chloride ($\frac{1}{10}$); it becomes positive during its movement in the liquid, and again becomes positive at the moment when it is withdrawn. The same effects are obtained with pure gold.

A silver wire, freshly amalgamated, gives in acidulated water the same effects, in point of direction of current, as platinum and gold, but with greater intensity.

In salt water amalgamated silver acts as in acidulated water, contrariwise to the behavior of platinum and gold.

The E. M. F. produced by movement is analogous to the E. M. F. of polarization. It is immediately destroyed in solutions of salts of the same metals as those used. Thus, electro-

lytic zinc gives no movement of the current in a slightly con-
centrated solution of zinc sulphate.   In a dilute solution of
the same salt the effects are very weak, and depolarization sets
in as soon as the metal is left at rest.   The same is true for
platinum in platinum chloride, copper in a salt of copper, and
silver in silver nitrate.

**Electric Currents produced by the Successive Immer-
sion of two Mercury Electrodes in a Liquid.**—Quincke
(1874) has reached the following results :

1. If two mercury electrodes connecting with a galvan-
ometer are plunged successively in an indifferent conducting
liquid (water, alcohol, glycerine, saline solutions, hydrochloric
acid, etc.), an electric current is observed which travels from
the freshly-moistened electrode to that which has been wet
for some time.

2. The intensity of the current decreases in proportion as
the resistance of the liquid column which separates the two
electrodes augments.

3. The E. M. F. developed varies according to the nature
and concentration of the different liquids.   It diminishes when
the concentration of the saline solution augments, and may
reach 0.06, the E. M. F. of a Daniell element.

4. This E. M. F. is greater as the contact is quicker between
the liquid and the electrode last immersed therein.   It thus
tends towards a maximum which is very quickly reached with
viscous liquids, such as glycerine.

5. The E. M. F. produced does not depend absolutely on
the magnitude of the constant of capillarity of the contact
surface between the mercury and the surrounding liquid.

6. The origin of these currents is probably due to a modi-
fication in its molecular state (concentration) which the liquid
gradually undergoes at its plane of contact with the mercury.

7. By successive immersion of two solid metal electrodes
in water or other liquids there is also produced an electric
current with mercury, and for the same reason.

8. Currents produced by the successive immersion of two
mercury electrodes in sulphuric acid, nitric acid, etc., are due

to the bodies developed by the chemical action produced on the mercury. They are therefore secondary phenomena or polarization currents.

Production of Electricity by Contact of two Metals.— Thomson arranges a copper funnel in proximity to a zinc cylinder, so that the end of the funnel will be located at a point at about the middle of the height of the cylinder. Copper filings are poured into the funnel and allowed to escape so that they flow past the cylinder surface without touching it.

It is found that at the place of contact of the copper and the zinc a difference of potential is produced, the copper being at a lower potential than the zinc.

Electricity produced between the Surfaces of Mercury, and Movements produced in Mercury by Deoxidation of that Metal.—In 1809 Ermann discovered that a globule of mercury in a tube of small diameter placed in contact with an electrolytic liquid became displaced when a current traversed the apparatus.

Lippmann attributed the electricity generated at a mercury surface in contact with acidulated water to a change in the capillary constant.

According to R. Sabine, this electricity may be explained by different states of oxidation of the ascending and descending surface.

Thus, electricity disengaged between surfaces of pure mercury which are not submitted to the action of hydrogen is due to different conditions of oxidation.

The movements observed in mercury electrodes under water or under dilute sulphuric acid are attributable to displacements of the surface corresponding to different atomic volumes of the metal and of its oxide. The author believes that capillary attraction is not an electric phenomenon.

Production of Electricity on Contact of Different Metals.—According to Exner (1880), the developing cause does not reside in the contact itself, but on the chemical influences exerted on the metals by the surrounding medium.

On theoretical considerations, he reaches the following con-clusion, namely : if by A the calorific equivalent of 1 Daniell be represented, and if by B be represented the heat of oxida-tion of zinc, for example, (referred to its atomic weight,) the difference of potential between the zinc and an inoxidizable metal (platinum) in air will be equal to $\dfrac{B}{2A}$.

If the metal connected to the zinc is itself oxidized by air, the difference of potential between the two metals will always be measured by half the difference of their heats of combus-tion.

The following results have been obtained, taking the Daniell element as unity :

	E. M. F. developed by the contact of two metals determined by experiment.	E. M. F. calculated by formula $\dfrac{B}{2A}$.
Zn, Pt..............	0.881	0.879
Cu, Pt..............	0.367	0.383
Fe, Pt..............	0.704	0.701
Aq, Pt..............	0.083	0.062

Electromotive Forces developed at the Contact of Metals and Inactive Liquids (Gaugain, 1872).—1. A plate of dry platinum plunged in distilled water is negative with rela-tion to a second plate already in the water.

2. A plate that is dry and hardened by rubbing is negative to another plate which is dry but softened by annealing. This may be considered as a consequence of the foregoing, since the hardened plate does not become so easily wet as the annealed plate.

Magneto-chemical Cell. — Balsamo (1867) placed two magnetized bars of like surface and weight in a solution of oxalic acid, one having its N. pole immersed and the other its S. pole. The first acted like the zinc, the second like the copper electrode in the ordinary voltaic cell, and a current was produced.

Disengagement of Electricity on Contact of Gases and of Incandescent Bodies (J. Elster and H. Geitel, 1883).— When air, or any other gas, is passed over incandescent platinum, the gas becomes charged with positive electricity and the platinum becomes negative.

The current produced may have an E. M. F. of 0.95 volt, and is more intense as the incandescence is higher.   Below redness there is no current.

If dry air be replaced by moist air, by carbonic acid, by oxygen, or by illuminating gas, the polarity of the disengaged electricity does not change, and even the potential difference remains constant and independent of the nature of the gas employed.

The nature of the cold electrode is not material.   Only, if, in place of a dry metal, a plate of wet metal be employed, the difference of potential which takes place between the metal and the liquid must be added to that which is examined, and will increase or diminish the deviation of the electrometer.

If the metal used is oxidizable, the E. M. F. between the metal and the oxide intervenes.   In case the gas employed is illuminating gas, there is gradually produced on the incandescent sphere a uniform deposit of carbon which diminishes the observed deviations.   The electrometer deviates the more rapidly as the hot gas or air current is more rapid.   According to Elster and Geitel, the gas electrified at the contact of the incandescent metal just as the plate of an electric machine electrifies at contact with the rubbers, and the cold electrode takes the place of the comb.

Does the Evaporation of a Liquid produce Electricity? —S. H. Freeman (1882) has evaporated different liquids—distilled, water alcohol, ether, solution of sea-salt, copper sulphate, etc., in metallic vessels.   No electricity was recognized by means capable of indicating a difference of potential of $\frac{1}{400}$ Daniell cell.   L. J. Blake (1883) reached a like conclusion.

When the Surface of Water is electrified, is the Vapor emitted charged with like Electricity?—Blake has strongly electrified water contained in a porcelain capsule, using a bat-

tery of 480 zinc-copper elements, one pole of which entered the water, the other pole being connected to earth or to the conductor of an electric machine. No electric signs appeared either with pure water, saline solutions, or mercury at temperatures up to 100° C.

Is the Condensation of Watery Vapor a Source of Electricity?—Volta (1799) observed by means of his electroscope that the condensation of watery vapor carried to the temperature of from 80° to 88° yielded a small trace of electricity. Saussiere and Reich (1846), on condensing watery vapor while avoiding all friction, could not recognize any disengagement of electricity. Palmieri (1862) was able by means of a condensing electroscope to recognize positive electricity of weak tension in the vapor of water condensed at high temperature above a platinum vessel. Kalischer (1883) resumed the same researches with more modern instruments, and even under more favorable conditions found no production of electricity. Kalischer remarks, however, that during his experiment the needle of the Thomson electrometer did not rest at zero, but moved to and fro irregularly. Palmieri in 1883 reached the same results obtained by him in 1862; but F. Magrini (1886), repeating his experiments, concluded that the positive electricity observed by Palmieri was probably frictional electricity, and that there was no perceptible disengagement of electricity through the condensation of the watery vapor.

Production of Electricity during Congelation of Water.—Grotthus (1825) noted that if water is very rapidly congealed in a Leyden jar the exterior coating of which is not insulated, a weak charge of electricity results: the interior of the jar is positive and the exterior negative. When ice is rapidly melted the inverse effects are observed, the exterior of the jar then being positively electrified.

Production of Electricity by the Occlusion of Hydrogen.—Kendall (1884) constructed a voltaic couple as follows: A platinum tube closed at one end and forming one electrode

has attached to it a glass tube which conveys into it hydrogen. The platinum tube is held in the middle of an ordinary platinum crucible which forms the other electrode. In the crucible various substances are melted at a red heat.

Melted borate of calcium gave an E. M. F. of 0.34 volt, and Berlin porcelain an E. M. F. of 0.65 volt. A current, though weaker, was obtained with phosphoric acid, and the chlorides of potassium, sodium, lithium, magnesium, calcium, barium, and strontium. The majority of oxidizing salts melted at red heat gave no current. The quantity of electricity produced, variable according to the substances employed, is proportional to the heated surfaces, and increases with the degree of temperature. A couple formed by a rod of metal (platinum or iron, for example) covered with melted glass on which a platinum plate is applied being heated in a flame yields a current. This is due to the extraction of the occluded hydrogen of the inner metallic wire by the oxidizing flame of the lamp on the exterior sheet of platinum. An inverse current is equally produced afterwards by submitting the platinum leaf to a reducing flame, the hydrogen being anew occluded by the interior metal.

Production of Electricity by the Decomposition of the Molecules of Combined Water.—According to Pouillet (1827), when water contains strontia or other bases the platinum capsule containing the solution becomes charged with an excess of positive electricity and the vapor becomes negative. On using water containing ammonia the vessel is negative, and the water which is vaporized with the ammonia is positive. If the water holds in solution 1 per cent or even less of sulphuric acid, the vessel is negative. With saline solutions there is likewise a production of electricity. The apparatus is always negative whether the salts be in a neutral, a basic, or an acid state. The vapor of water is constantly positive. It is to be noted, however, that by evaporation only of distilled water no electric signs are obtained.

Influence of the Dissolved Substance on the Sign of the Electricity developed.   (Gaugain, 1854.)

Dissolved Substance.	Charge transmitted by the Platinum Crucible to the Electroscope.
Potash ....Strongly positive.	
Soda .... "	
Baryta .... "	
Strontia .... "	
Lime ....Weakly positive.	
Ammonia...................... " negative.	
Sulphuric acid, concentrated.......None.	
" " dilute ....Weakly negative.	
Acetic acid, concentrated or dilute...None.	
Nitric acid, concentrated..........None.	
" " dilute..................Weakly negative.	
Hydrochloric acid, conc. or dilute... " "	
Boric acid........................Strongly "	
Phosphoric acid.................. " "	
Sodium chloride................. " "	
Barium chloride.................. " "	
Potassium sulphate..............Weakly positive.	
Sodium......................... " negative.	
Magnesium .... " "	
Sodium phosphate................Strongly "	
" borate ....Weakly "	
Potassium nitrate................ " "	
Sodium " ....Strongly "	
Barium " .... " "	
Strontium " .... " "	
Potassium carbonate.............. " positive.	
" chlorate ....Weakly negative.	

According to Gaugain, the electricity which is manifested during the evaporation of aqueous solutions is due exclusively to the friction between the water and the sides of the vessel, or between the water and the deposits lining the water, or between the vessel and dust projected thereon from without.   These

last two causes appear always to produce electricities of different signs. The first two develop electricities sometimes of like, sometimes of unlike, name. The friction with the deposits formed on the interior of the vessel appears to be most energetic.

Buff (1854), experimenting successively with water, sodium chloride, a potash solution, dilute sulphuric acid, and dilute nitric acid, has found that the vapors are always electrified, as the liquid would be by its contact with an immersed metallic wire. Thus taking nitric acid and a platinum wire, the vapor is strongly negative. As is well known, nitric acid by its contact with platinum becomes charged with negative electricity.

Electricity developed during Evaporation of Liquids (Tait and Wanklyn, 1862).—The following table gives a list of the substances tested, with the E. M. F.'s of the electricity which each frees at the moment when the crepitating noise immediately following cessation of the spheroidal state begins. The indications are in electrometer degrees; 5°.8 representing the E. M. F. of 1.96 volts.

Bromine.......................................	$+$ 400°
Iodine........................	$+$ 90°
Ethyl bromide ....Hardly perceptible.	
Methyl iodide, $+$ in several experiments; $-$ in 3 experiments.	
Benzine......................................No effect.	
Ethyl valerianate...................... ....No effect.	
Ethyl oxide (ordinary ether) ....Very weak, doubtful.	
Chloroform............. — if the plate is hot; $+$ if it is cold.	
Ammonia...............................	200°
Alcohol	$-$ 10°
Mercury	$-$ 75°
Chloride of sulphur.............................	$-$ 100°
Distilled water containing a trace of carbonic acid .	$-$ 80°
Concentrated solution of potassium carbonate.....	$-$ 310°
" " " caustic soda.............	$-$ 40°
Dilute solution of caustic soda	$-$ 25°
Concentrated solution of caustic potash	$+$ 150°

Concentrated nitric acid .... $+$ $7°.5$,
Nitric acid (1 part acid, 4 water)................ $-$ $35°$
Concentrated hydrochloric acid .... $-$ $160°$
Dilute   "   "   .... $-$ $50°$
Concentrated sulphuric acid .... $+$ $15°$
Concentrated solution of sodium chloride .... $-$ $400°$
    "   "   " potassium iodide........ $-$ $80°$
    "   "   " copper sulphate......... $-$ $1000°.2$
Sol. double oxal. chromium and potass.... Hardly perceptible.
Concentrated solution of iron chloride.........Negative effect.
Monohydrated acetic acid .... $+$ $3°$
Anhydrous   "   "   .... $-$ $9°$

Production of Electricity by Immersion in Liquids of Metals unequally heated (Gore, 1857).—If two plates of similar metal be placed in a liquid conductor, a current is obtained when the two parts of the liquid which wet the plates are at different temperatures, or when one plate is kept at a temperature higher than that of the other.

By using two platinum plates, Gore has found that hot platinum is positive relatively to cold platinum in acid liquids, and that it is negative in alkaline liquids. The sole exceptions are the following: in aqua regia and hydrocyanic acid the hot platinum is negative, which is explained by a preponderating chemical action; hot platinum is slightly positive in neutral sulphate of soda; it is easily negative in bitartrate of soda, which gives, however, an acid reaction.

The other metals act like platinum, provided the chemical action be eliminated or sufficiently diminished; and in all cases this chemical action acts in inverse direction to the other action, depending on the difference of temperature. The current does not further result in a thermo-electric action of the different metallic parts of the circuit.

Production of Electricity by the Action of Acids and Saline Solutions on Metals.—Becquerel has determined the following laws:

1. When an acid reacts on a metal the acid takes positive and the metal negative electricity.

2. The unattacked metal is always positive.

3. If both metals are attacked by the liquid, that which is most attacked takes negative electricity.

According to Becquerel and Matteucci, there will be disengagement of electricity during chemical action only to the extent that the two bodies in presence of one another are electrical conductors; thus in the combination of a metal with oxygen, iodine, or a dry bromine there is no production of electricity.

L. Palmieri has, however, observed that the combination of two simple bodies (metal with metalloid, or two metalloids, like phosphorus and iodine) disengages electricity.

There are several exceptions to Becquerel's second law: If two vessels filled with a solution of copper nitrate be connected by means of a cotton wick, and if in each of them the end of a copper plate be plunged, no current will be observed; but if a drop of nitric acid be placed in one of the vessels, the copper therein becomes negative.

Tin and its sulphate, iron and its chloride, lead, antimony, and bismuth, behave the same as copper in regard to their solutions when a few drops of acid are added thereto. The same is true of zinc or iron with solutions of their nitrate. The metal takes positive electricity in conformity to the general law; but with solutions of their sulphates these two last-named metals sometimes produce inverse effects; the metal becoming positive as soon as a few drops of sulphuric acid are added. (Becquerel.)

On the other hand, if the cell be formed in the following manner: zinc, solution of zinc sulphate; porous cup, aqua regia (1 part nitric acid and 4 parts hydrochloric acid), the singular fact is observed, which appears to be in contradiction to the electro-chemical theory of the cell, namely, that the zinc which enters the solution of zinc sulphate, and which, consequently, is hardly attacked at all, is negative in relation to the zinc immersed in the aqua regia, which, on the contrary, is

strongly attacked. In other words, the zinc which is immersed in its sulphate behaves the same as the zinc of the Bunsen element, while the zinc which is immersed in aqua regia acts like the carbon. (Mauri, 1881.)

Production of Electricity due to the Mutual Actions of Solutions.—Becquerel has formulated the following principles :

1. In the mixture of acids with water, or in their combination with it, the water acts like a base, while it acts like an acid with regard to their alkaline solutions.

2. Concentrated solutions of neutral salt act, with regard to water and with respect to the electric effects produced, like the acids in relation to the bases.

3. Acids in their combination or mixture with other acids behave in such a way that the more oxidizing acids are the most electro-positive. Acids in their combinations with bases appear to keep the same property, so that in the reaction or the mixture of two saturated solutions of neutral salt, the nitrate is positive with regard to the sulphate, the sulphate with regard to the phosphate, etc.

4. When several solutions, acid, neutral, or alkaline, are placed one beside the other, so that they mingle very slowly, the electric effects produced are the resultants of the individual effects which take place at each surface of contact.

5. Contrary to the opinion of Volta, an electric chain, or rather a closed circuit, can be formed of liquids only in which a current circulates, and whence result phenomena of decomposition and recomposition if bodies which are conductors of electricity exist in the circuit.

Volta showed that when several substances, solid or liquid, are in contact one with the other, the electric effects are the same as if the extreme substances were in immediate contact.

Disengagement of Electricity by the Oxidation of Metals by the Action of Heat (Becquerel).—The following systems have been found to produce electricity :

1. Crucible containing a mixture of dried sodium carbonate

and crushed glass, the whole heated to a temperature of fusion. Electrodes are respectively copper and iron.

2. An iron tube containing a glass tube in which is a copper cylinder. After all the interstices of the apparatus are filled with crushed glass, it is highly heated.

Disengagement of Electricity produced by the Action of Water on a Saline Solution (Becquerel and Bucholz).— A metallic solution, as neutral as possible, such, for example, as copper nitrate or sulphate, was placed in a test-tube. Distilled water or acidulated water was then poured in very carefully, so that the two liquids remained separated by their gravity. The copper plate then being inserted, it was found, some hours afterwards, that the end plate which was in contact with the metallic solution became covered with the copper deposit.

Other metals, such as zinc, iron, and tin, with a solution of their respective sulphates and water, showed the contrary effect ; the end which was plunged in the metallic solution becoming the positive pole and oxidized instead of being covered with metallic deposit.

On using a concentrated solution of these metals and a solution which is not concentrated, the deposit is formed on that part of the metal which enters the solution last named.

Examples: 1. Solution of stannous chloride, water, tin plate. The metallic deposit is formed on that part of the plate which enters the water.

2. Solution of cuprous chloride in hydrochloric acid, water, copper plate. The metal deposit is produced on that part of the plate which enters the water instead of on the lower portion, as in the case of the nitrate or sulphate.

Electromotive Forces of Molecular Voltaic Couples which produce the Development of Wet Collodion Photographic Proofs.—In 1877 Lermantoff demonstrated by experiment that the development of photographic proofs on moist collodion is an electrolytic process, each molecule of metallic silver produced by light on the sensitive surface forming a voltaic element with a molecule of silver nitrate and a

molecule of iron sulphate of the developer. The result of the electrolysis is a deposit of silver on the metallic molecule.

Disengagement of Electricity by Immersion of Carbon in a Saline Solution (Moride).—If, in a solution of copper nitrate or sulphate, or silver nitrate or sulphate, a piece of carbon, either incandescent or previously extinguished in water, be immersed, the carbon will become covered with copper or silver. It will be electrified negatively and the liquid positively.

Disengagement of Electricity produced on the Contact of Earths and Saline Waters.—Salt water acts, with regard to the earth, like soft water; that is to say, the water is negative relatively to the earth. Whatever may be its areometric degree, the presence of salt in the earth causes it to lose its positive character. (Becquerel.)

Production of Electricity in Chemical Decompositions. —Sodium bicarbonate placed in a red-hot capsule decomposes with production of carbonic acid. The capsule is electrified positively, while the acid carries with it negative electricity.

On heating a platinum plate of silver oxalate this salt decomposes rapidly, leaving silver behind which becomes positively electrified.

According to Peltier, there is required the oxidation of one hundred and fifty-one billionths of a milligram of zinc (0.000000000151 mg.) in order to produce dynamic electricity capable of causing a deviation of 1° of the needle of a sensitive galvanometer, and the oxidation of a tenth of two thousand one hundred and thirty-six quadrillionths of a milligram of zinc (0.00000000000002136 mg.) in order to produce static electricity capable of causing a divergence of 1° of the needle of his electrometer.

According to Faraday and Becquerel, in order to decompose 1 milligram of water there are required 20,000 discharges of a battery having a surface of one metre square, or the discharge of a condenser having two hectares of surface.

Electricity produced by the Disengagement of Gases. —Lavoisier, Laplace, and Volta (1781) were the first to observe,

by means of Volta's condensing electrometer, a disengagement of electricity during the production of hydrogen by the action of dilute sulphuric acid on iron filings.

Henkel (1884) has observed, using a gold-leaf electrometer, that—

1. " When dilute acid (sulphuric or hydrochloric) is poured on zinc or iron, the disengaged hydrogen carries with it positive electricity, while the liquid shows an excess of negative electricity.

2. If the hydrogen-bubbles, instead of being rapidly disengaged, remain in the acid liquid, they yield to it their positive charge, and then, on becoming free therefrom, take away negative electricity from the liquid, leaving the latter more positive than before.

3. When the attack has lasted a certain number of minutes, zinc being used, the metal becomes covered with a blackish coating, which forms the positive pole of a local couple of which the zinc is the negative element.   In this case the gas which is given off takes negative electricity and the liquid becomes positive.

4. With iron the attack is slower and the effects weaker than with zinc.   Otherwise the same peculiarities are presented.

5. When calcium carbonate is attacked by hydrochloric acid, negative electricity is given off ; but here also the electric phenomenon ordinarily ends with a change of sign after some time."

Production of Electricity by Combustion.—By placing vertically a cone of carbon in communication with earth below the lower plate of a condensing electroscope and on lighting the upper part, positive electricity is collected from the carbonic acid gas.   The same result can be obtained by combustion of carbon in pure oxygen so long as the gas is not dry.

During the combustion of bodies oxygen takes positive, and the combustible negative, electricity.   In order to observe the phenomenon it is necessary that the bodies should be con-

ductors. Thus the production of electricity may be noted with carbon, but not with sulphur. (Pouillet.)

According to Matteucci (1845), there are no signs of tension nor of electric current in the combination of two different elementary molecules, nor in the separation of these molecules combined. In order that these signs may appear, the chemical action of one elementary molecule on a combination of two others is necessary. In this action one of the latter tends to separate itself, or actually separates and becomes free, while the other tends to combine, or actually combines, with the first.

The electric signs thus obtained are at their maximum if the two elements of the combination or of the electricity are in presence of two elements, not combined together, which tend to seize upon the elements of the electrolyte.

If, in the combustion of carbon, electricity is disengaged, as Pouillet has observed, this is due to the fact that ordinary carbon always contains hydrogen, which burns with the carbon and forms water. Now, burning carbon decomposes at this temperature water which it finds thus formed by the combustion of the carbon itself, and the chemical action resulting therefrom produces the current.

"If," says Matteucci, "graphite or diamond could be burned in oxygen entirely deprived of water, no sign of electricity would be observed."

Palmieri has found that with bisulphide of carbon, benzine, petroleum, and the vegetable oils, a flame from these bodies shows positive electricity when the capsule in which the burning occurs is connected to the earth, or that the capsule shows negative electricity when connected to a condenser if there is placed in the flame a plate or wire of platinum in communication with the earth.

With liquids the flames of which form on platinum a carbon deposit, less electricity and very often inversions of direction are observed.

But if simple bodies or compound bodies be burned, such as sulphur, phosphorus, magnesium, paper, and starch,

operating in the same way, contrary effects are noted; that is to say, the flame shows positive electricity and the combustible, as well as the platinum capsule which it contains, gives negative electricity. Thus in the combustion of a simple solid body, the flame is positive and the combustible negative.

Palmieri has examined the conditions of combustion of a simple gas, hydrogen.

Before lighting the gas, he directed a jet of it against a plate of platinum connected to a condenser, and after having observed that no electrical sign then appeared, he lit the gas The flame then showed negative electricity, and when for the plate a bent wire drawn to a point was substituted, it was possible to collect positive electricity constantly at the point.

It appears to be demonstrated that in the combustion of all bodies two different electric states are developed. When these last exist simultaneously, they neutralize one another, and hence they generally cannot be found; but if arrangements be made so that one of the electricities is caused to disappear, the other is set at liberty.

Electromotive Force of Combustion (H. Pellat, 1885).— The end of a Bunsen burner was placed inside of a large hollow metal cylinder closed above by a plate of the same metal so that no draught opening was left. Pellat calls this cyllinder an " inductor," and the apparatus acts exactly like a voltaic couple. If to the inductor and to the burner two wires of the same metal be connected, a constant difference of potential in a state of electric equilibrium may be noted between them, which is rapidly re-established whenever disturbed, thus producing an electromotive force of the element.

These cells may be connected in the ordinary way like electro-chemical cells.

The E. M. F. depends on the nature of the gas which is burned, on the nature of the metal which constitutes the burner, and on the nature of the internal surface of the conductor.

The following figures have been obtained for several couples:

Hydrogen gas, brass burner, copper inductor...... 0.30 volt.
 " " " " zinc " ...... 0.58 "
 " " zinc " copper " ...... 0.09 "
 " " platinum " " " ...... 0.45 ' "
 " " " " platinum " ...... 0.10 "
Illuminating " " " " " ...... 0.94 "
 " " " " copper " ...... 1.72 "

The burner is positive and the inductor is negative.

Electricity of Flame (Elster and Geitel, 1882).—The E. M. F. is independent of the size of the flame.

It depends on the nature of the metal which forms the electrodes and the nature of the gases in combustion. Flames may be connected in series like the cells of a battery.

According to Elster and Geitel, the theory of the electric properties of flames is, briefly, as follows: The gases of the flame and of the air which immediately surround it act like electrolytes with regard to electrodes immersed therein; and to this source of electricity is to be added the thermo-electric effects due to the incandescent states of the electrodes.

Electricity developed in an Alcohol Flame submitted to the Action of a Blow-pipe (Grove, 1854).—The electrodes are formed of two platinum spirals, one of which is placed in the lower and the other in the upper part of the flame. Chemical action begins at the lower spiral, which takes the place of the zinc in the cell, and the upper spiral acts like the conducting metal.

The electricity then developed is not due to a thermo-electric current, but rather to the chemical action produced by the combustion of the alcohol. In fact, the thermo-electric current which would be caused under these circumstances would move in opposite direction to the current developed by combustion.

Electricity of Plants.—Buff (1854) has deduced from his observations the following general rule:

Roots, as well as all portions of the interior of plants con-taining sap, are constantly in a state of negative electricity, while the moistened surface of green branches, as well as that of leaves, flowers, fruits, are, on the contrary, permanently positively electrified.

The electroscopic indications produced by the electricity of plants are, however, very weak; and even with the most delicate instruments it is difficult to obtain sufficient charges to prove with certainty that they are due to the plant itself. Buff, by forming a compound circuit of plants, connecting them in series, succeeded in obtaining more perceptible effects. Every healthy leaf with its extremity cut off acts, so to speak, like a voltaic element, and a compound circuit may be formed by arranging a number of these in series. Buff claims to have produced with a battery of twelve leaves an E. M. F. a little greater than half of that developed by a single couple of zinc and copper immersed in pure water.

Baconio, in 1807, constructed a cell of disks of walnut-wood and disks of beet-root, using for an exciter a leaf of cochlearia, and obtained effects sufficient to influence a frog-leg electroscope.   •

The wooden disks were deprived of their resinous principle by a prolonged digestion in a mixture of vinegar and cream of tartar.

Electricity of Fish.—The extraordinary modification of the peripheral extremities of nerves by which electricity is generated and discharged is found in four genera of fishes, as follows: (1) The Torpedo. This is the generic and popular name of the electric rays or skates of the family *torpedinæ.* The electrical apparatus is arranged in two masses, one on each side of the skull, between this and the base of the pectorals. It is composed of a multitude of perpendicular gelatinous columns or hexagonal prisms, separated by membranous par-titions containing a fluid freely supplied with blood and receiv-ing very numerous nervous filaments from the par vagum and trifacial nerves. There are about twenty species of torpedo, arranged in seven genera, in the seas of all parts of the world.

Actual contact with the torpedo is not essential. The shock is felt through water, even when dashed on the fish, circuit being completed through the earth to the ventral surface. The dorsal surface is positive, and the ventral negative.

(2) The electric eel (*gymnotus electricus*, Linn.) is an inhabitant of the rivers of the northern parts of South America. The electric apparatus consists of four organs, two on each side, composed of an assemblage of membranous horizontal plates nearly parallel and intersected by delicate vertical plates. There are about 240 cells thus formed to the square inch, filled with gelatinous matter. The electric eel seems to be a mere appendage to the anterior part of its battery for moving it about, all of the other organs being confined in a very small space. The shock of the gymnotus, according to Faraday, is equal to that of 1500 Leyden jars of 3500 square inches of surface.

(3) A fish of the family *siluridæ* and genus *malapterurus* (Lacép.), found in the Nile and elsewhere in Africa. Its electrical organ is a combination of the structures of the torpedo and the gymnotus. The shock is comparatively feeble. (4) A fish of the order *plectognathi*, family *diodontidæ*, and genus *tetraodon* (Cuv.), found in the lagoons of the Pacific, the electric power of which is also weak.

In all these fishes the generation of the current is apparently due to nervous action. It behaves like electricity from any other source, energizing magnets, producing the spark, etc. The electric like the muscular power is exhausted by exercise and restored by rest. Late investigations on electric fishes are wanting. These creatures are of the highest scientific interest inasmuch as they are strictly natural machines for the direct conversion of chemical energy or chemical and heat energy combined into electrical energy—just as the glowworm is a machine for the direct conversion of chemical energy into light without heat.

CHAPTER XXV.

THE BIBLIOGRAPHY OF THE VOLTAIC CELL.

THE following list, compiled from the indexes of the " Park Benjamin Electrical Library," contains the principal works relating to the voltaic cell. It is by no means a complete bibliography of the subject, for such—including as it does an immense number of papers, reports, etc., read before learned societies the world over—would occupy far more space than can here be afforded. Most of these publications are, however, referred to in the works below named—especially in the elaborate lists given by Becquerel, De la Rive and Du Moncel— so that for any ordinary "state of the art" examination the student has here sufficient data properly to direct him. For closer lines of investigation reference may be had to Poggendorff's admirable *Biographisch-Literarisches Handwörterbuch zur Geschichte der Exacten Wissenschaften* (Leipsic, 1863 *et seq.*); to the *Catalogue of the Ronalds Library* (London, 1880), which, however, contains many inaccuracies; to *A Bibliography of Electricity and Magnetism*, 1860 to 1883, by G. May (London and Leipsic, 1884), which supplements the Ronalds catalogue; to P. F. Mottelay's *Chronological History of Electricity* (" Electrical World," N. Y., and " Engineering," London, 1892); and to the *Bibliografia Italiana di Elletricità e Magnetismo* (Padua, 1881), which is very valuable for its references to little-known Italian works. Of course, all the general treatises and textbooks on electricity contain chapters on the voltaic cell, so that it is needless to name them; those which the author has found especially useful are, however, noted. Special indexes to

the electrical patents are now published by the United States Patent Office, and these supplemented by the British Patent Office Abridgments and Fournier's Digest of French Patents (named below) will greatly assist in researches in the archives of the three principal patent offices of the world. The most complete information concerning early researches on accumulators ("storage" cells) will be found in the printed records of the various patent litigations in the United States courts between the Julien Electric Company, the Electrical Accumulator Company, and the Brush Electric Company, which continued for nearly a decade prior to 1892.

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